Supporting Information

Formation and structures of Au-Rh bimetallic nanoclusters supported on a thin film of Al_2O_3/NiAl(100)

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Figure S1 shows the RHEED patterns, obtained at azimuth [0-10] and [0-11], for 2.0 ML Au deposited at 300 K and annealed to 450 K on the thin-film Al_2O_3/NiAl(100). The reflection rods of the RHEED patterns are ascribed to the oxide and the NiAl(100) substrate; the half-order reflections in Figure S1a are attributed to the (2 × 1) structure of ordered θ-Al_2O_3.[1-4] Additional patterns superimposed on the reflection rods at both azimuths [0-10] and [0-11] are from structurally ordered Au clusters. The Au clusters have their (001) facets parallel to the oxide surface and their [110] axes along direction [010] of the oxide surface, denoted as Au(100)[110]//Al_2O_3(100)[010]; the Au clusters have a mean lattice parameter 4.2

± 0.1 Å, expanding about 3 % with respect to bulk Au.

Figure S2 exemplifies the STM images for the morphological evolution of Au-Rh bimetallic clusters on thin-film Al_2O_3/NiAl(100) with annealing. They are from Rh(0.7 ML)/Au(0.65 ML) bimetallic clusters annealed to 450 (a), 570 (b) and 750 K (c), respectively. Compared to the bimetallic clusters as prepared at 300 K (Figure 1c), the mean diameter of the bimetallic clusters annealed to 450 K decreased slightly but the mean height remained the same (Figure S2a). Although the size decreased, the cluster density increased; the total quantity of the deposited metals remained the same. The size variation results from limited ripening: the clusters were dissociated slightly at 450 K and the atoms from the dissociated clusters formed new clusters, rather than joining the existing clusters, due to abundant preferential nucleation sites, the linear protrusions on the Al_2O_3/NiAl(100). While annealing to 570 K, the size altered little whereas the cluster density decreased (Figure S2b). Some metal atoms began to diffused into the substrate. On increasing temperature to 750 K, the size distribution become much broader and the mean diameter increased — a significant feature of sintering (Figure S2c). The cluster density and total quantity of deposited metals also decreased significantly; a significant proportion of metal atoms diffused into the substrate. The altered substrate structure was reflected on the RHEED patterns.

Figure S3 exemplifies the RHEED patterns for the annealing-induced structural alternation of Au-Rh bimetallic clusters on thin-film Al_2O_3/NiAl(100). The patterns are from Rh(1.0 ML)/Au(1.0 ML) bimetallic clusters annealed to 450 (a) and (b) 750 K, respectively. The RHEED patterns from the bimetallic clusters annealed to 450 K are the same as those as prepared at 300 K (Figure S3a). Red circles are drawn in the figure to denote reciprocal-lattice points for the bimetallic clusters Au-Rh(100)[110]//Al_2O_3(100)[010]. On annealing to 700 K, the patterns altered significantly; strongly modulated intensity along the reflection rods from the Al_2O_3/NiAl(100) appeared (Figure S3b). They indicate three-dimensional

scattering from the substrate — roughening of Al_2O_3(100) and NiAl facets.[5,6] As the oxide surface remained flat (Figure S2c), the roughening occurred under the oxide surface and at the oxide-NiAl interface. The incorporation of Au and Rh atoms into the substrate and their strong interaction with the substrate change the structural.[5,6]

Figure S4 shows the adsorption structures of Rh and Au atoms on the Al_2O_3(100), Rh(100) and Au(100) surfaces. Both atoms are preferentially adsorbed on the hollow sites of the surfaces.

The thermodynamic stability of the Au-Rh bimetallic clusters was examined by the calculations of segregation energies (E_{seg}) of the model surfaces. E_{seg} is the energy required to move the foreign elements, Rh in Au(100) or Au in Rh(100), from surface to subsurface; it is defined as

$$E_{seg}(\mathrm{Rh}) = E_{Rh,\ surface} - E_{Rh,\ subsurface}$$

$$E_{seg}(\mathrm{Au}) = E_{Au,\ surface} - E_{Au,\ subsurface},$$

where $E_{Rh,\ surface}$ and $E_{Rh,\ subsurface}$ are the total energies of the modelled Au(111) with a Rh atom replacing a Au atom at the surface and subsurface layers, respectively. Similarly, $E_{Au,\ surface}$ and $E_{Au,\ subsurface}$ are the total energies of the modelled Rh(111) with a Au atom replacing a Rh atom in the surface and subsurface layers, respectively.

The positive E_{seg}(Rh), 0.67 eV, and negative E_{seg}(Au), -1.24 eV, indicate that the Rh atoms prefer to locate at the subsurface whereas the Au atoms at the surface layers. Accordingly, the Rh layer likes to sink into the subsurface and squeeze Au out to the surface in Rh/Au clusters; the Au layer stays preferentially at the surface, forming Rh core-Au shell structure, in Au/Rh cluster.

References

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Figure S1

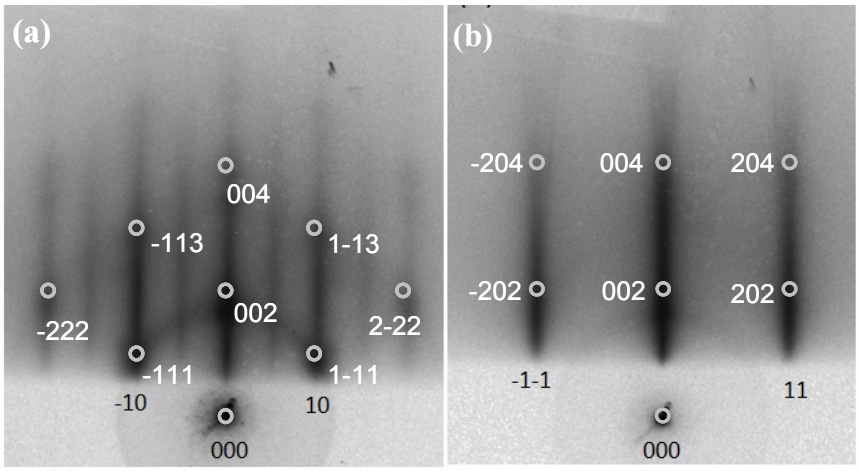

Figure S1 RHEED patterns obtained at azimuth [0-10] (a) and [0-11] (b) for 2.0 ML Au deposited at 300 K and annealed to 450 K on the thin-film Al_2O_3/NiAl(100). Grey circles in (a) and (b) denote reciprocal-lattice points for the clusters Au(100)[110]//Al_2O_3(100)[010].

Figure S2

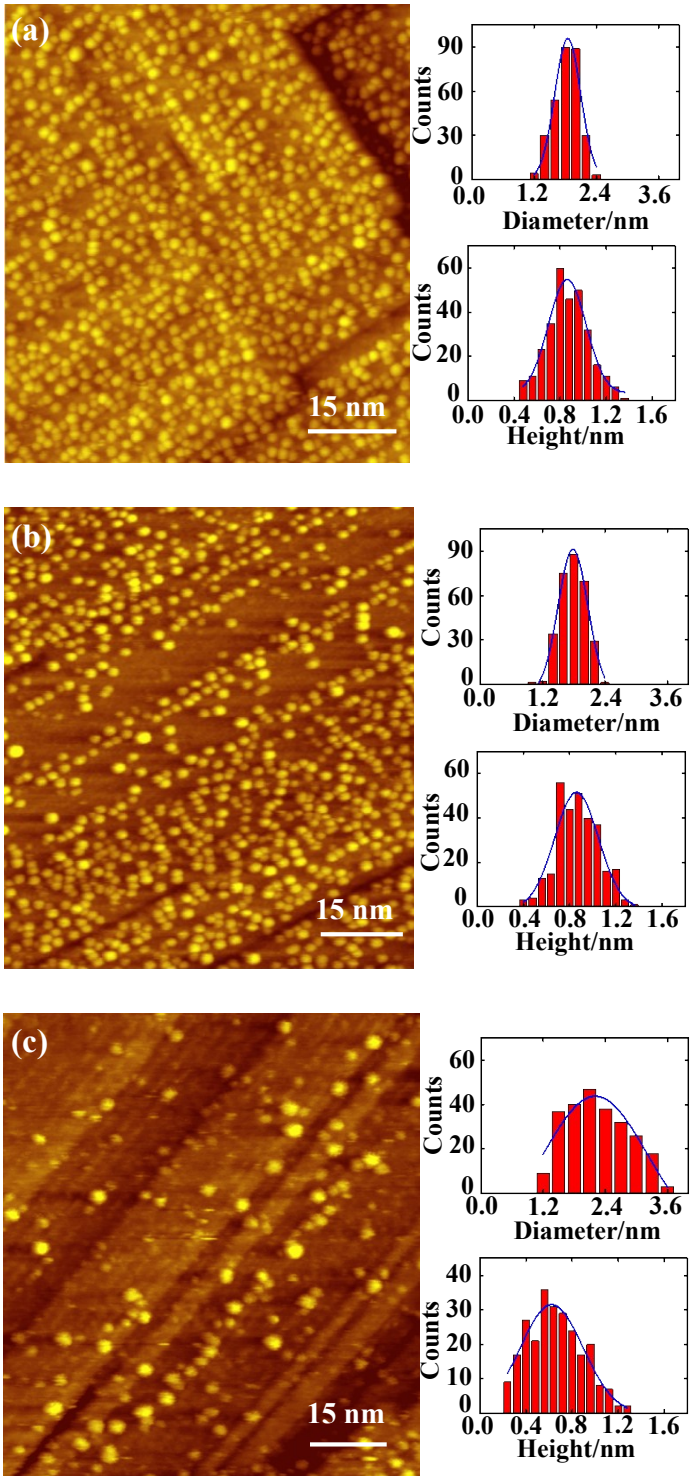

Figure 2S STM images of Rh(0.7 ML)/Au(0.65 ML) bimetallic clusters annealed to (a) 450, (b) 570 and (c) 750 K. The insets of each figure show histograms of the diameters and heights of the clusters. The bimetallic clusters were grown on thin-film Al_2O_3/NiAl(100) at 300 K.

Figure S3

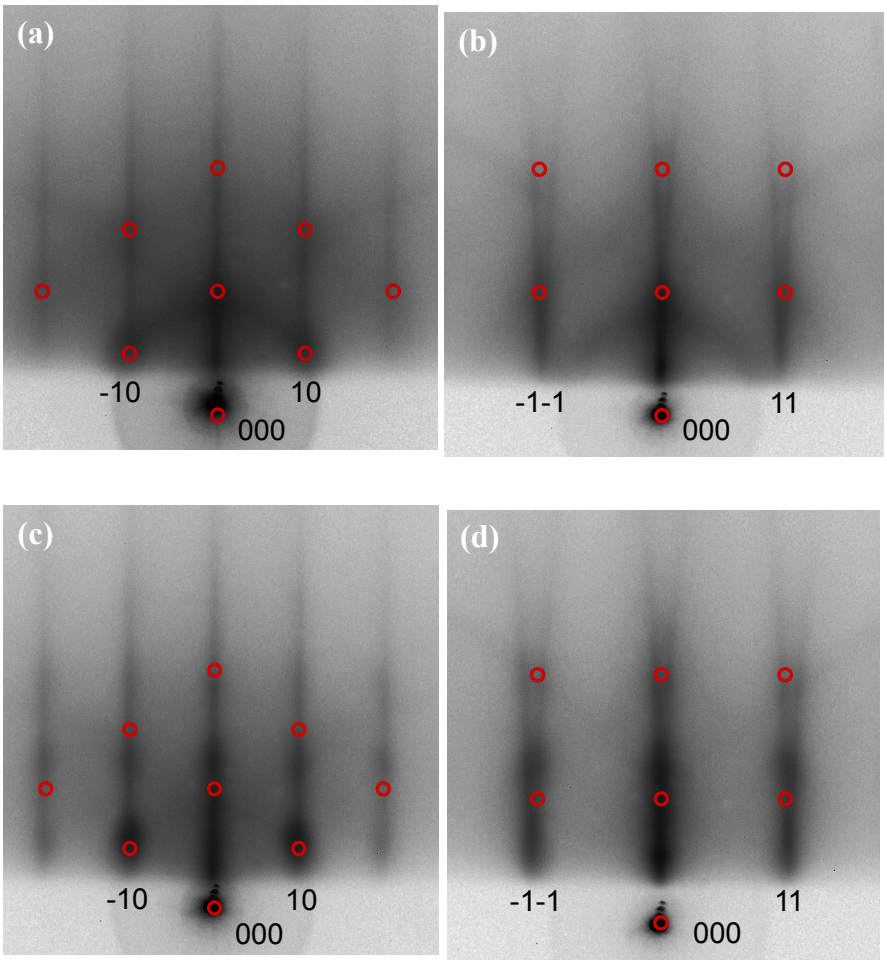

Figure S3 RHEED patterns for Rh(1.0 ML)/Au(1.0 ML) bimetallic clusters on thin-film Al_2O_3/NiAl(100) annealed to (a), (b) 450 and (c), (d) 750 K. (a), (c), shows patterns obtained at azimuth [0-10]; (b), (d), show patterns obtained at azimuth [0-11]. The bimetallic clusters were grown on thin-film Al_2O_3/NiAl(100) at 300 K. Red circles in (a)-(d) denote reciprocal-lattice points for the bimetallic clusters Au-Rh (100)[110]//Al_2O_3(100)[010]

Figure S4

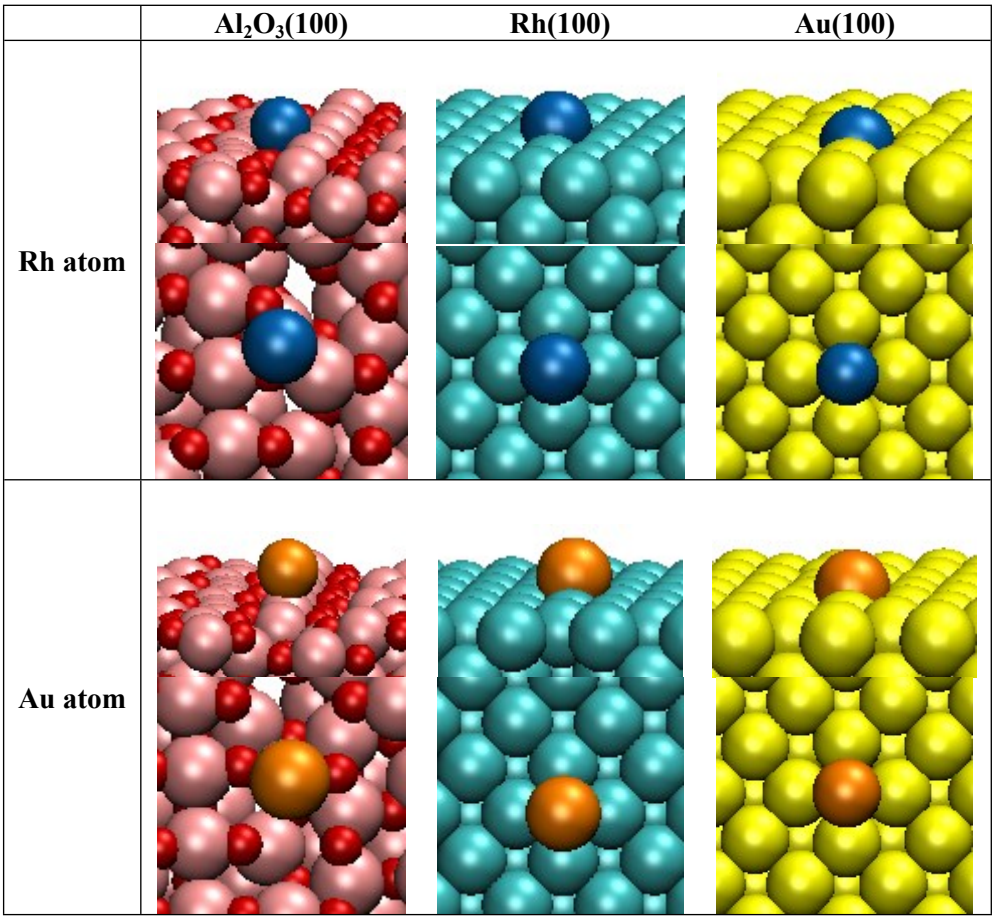

Figure S4 Top and side views of the adsorption structures of Rh and Au atoms on the Al_2O_3(100), Rh(100) and Au(100) surfaces, as indicated. The blue and orange spheres represent surface Rh and Au atoms, respectively. The pink, red, cyan and yellow spheres represent substrate Al, O, Rh and Au, respectively.