Science Advances
AAAS

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Supplementary Materials for

Unraveling the atomic structure, ripening behavior, and electronic structure of supported Au_{20} clusters

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Published 3 January 2020, *Sci. Adv.* **6**, eaay4289 (2020)
DOI: 10.1126/sciadv.aay4289

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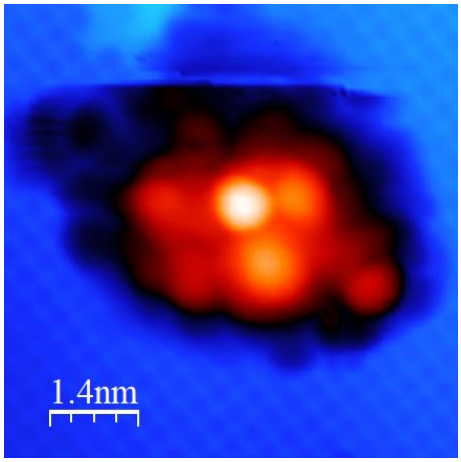

Fig. S1. Additional (next to Fig. 1, B and C) STM topography image of a Au_{20} cluster on 3L NaCl/Au(111), imaged with a Cl-functionalized tip. This image shows one protruding atom, but no clear tetrahedral feature. Tunneling condition: $V = -2$V, $I = 0.02$ nA.

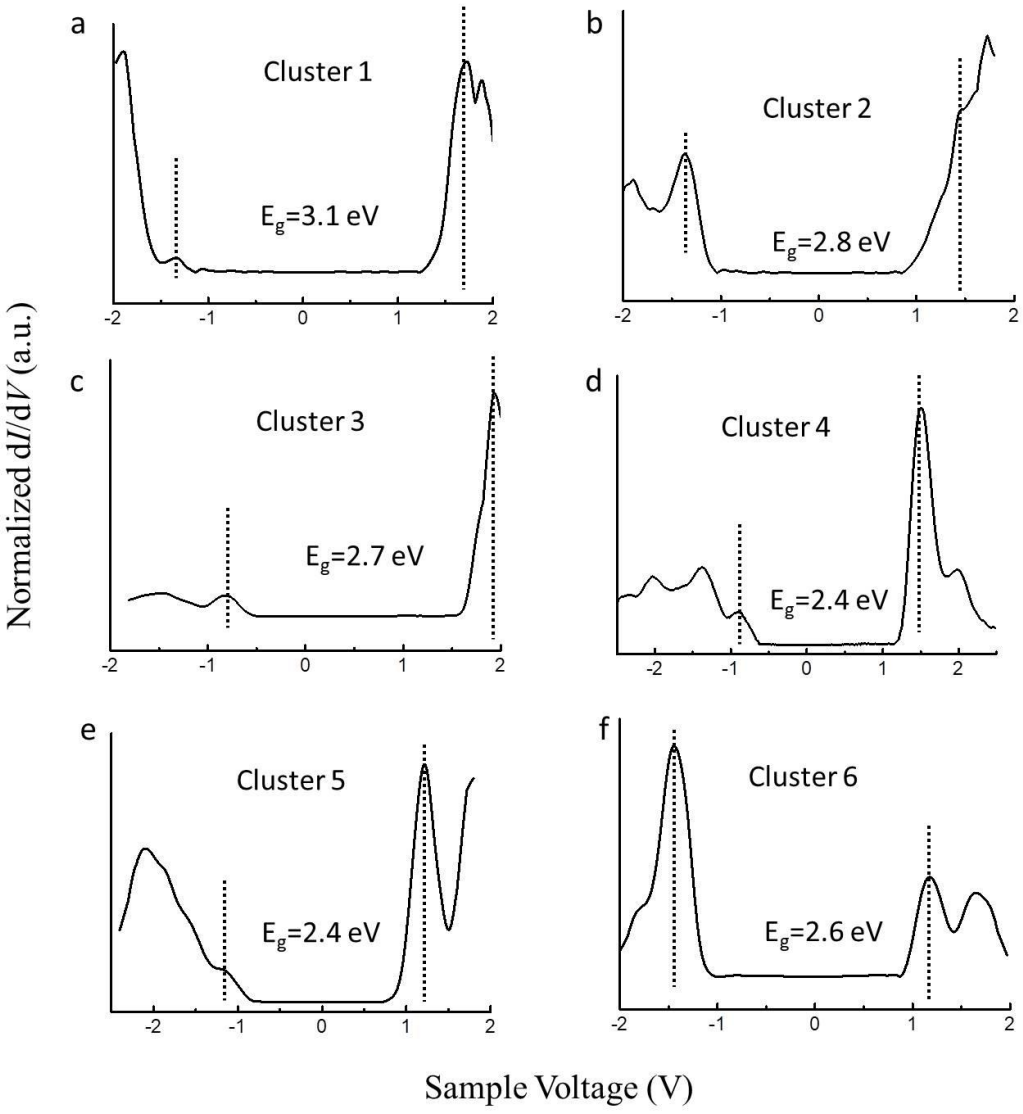

Fig. S2. Series of *dI/dV* spectra recorded on different Au_{20} clusters with different conditions of STM tip apex. Before performing the dI/dV measurements, the tip is modified on a bare Au(111) region. During searching for clusters in a large scanning area (typically 200 × 200 nm^2), the tip accidentally changes. So change of the tip apex for different Au_{20} images cannot be avoided. The size of the energy gap (E_g) around the Fermi level (0V) is indicated in each figure.

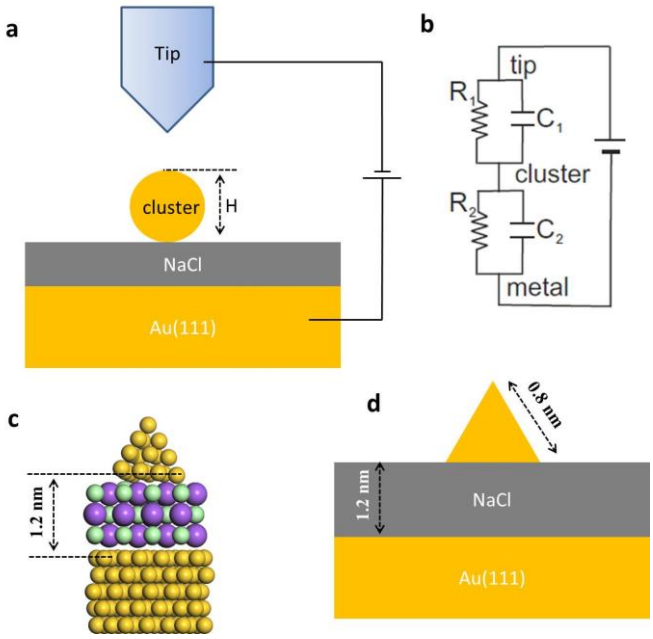

Fig. S3. Electrostatic model to estimate the capacitance of Au_{20}/NaCl/Au(111) system. a, Scheme of the STM tip scanning on a cluster on NaCl/Au(111). **b**, Equivalent electronic circuit of the tip-cluster-Au(111) double barrier tunnel junction in **a**. **c**, Simulated structures of Au_{20} on 3L NaCl/Au(111). **d**, Model used for calculation of the capacitance C_2 between Au_{20} and Au(111), where Au_{20} is modeled as an ideal tetrahedron. The edge of Au_{20} is 0.8 nm, which is consistent with the edge length obtained from the atomic model in Figure S3c/Figure 2(A). We assume that the gap between the Au_{20} metallic pyramid and the Au(111) metallic surface is completely filled with the NaCl dielectric material. Note that in the atomic model in Figure 2(A), the distance between the top Au atom and the NaCl surface is 0.94 nm because there is an additional gap of 0.29 nm between the bottom Au atoms and the top NaCl layer. The dielectric constant ε=5.5 *(42)* of bulk NaCl is used. Dimensions for NaCl: 30 nm ×30 nm ×1.2 nm; Dimensions for Au(111): 30 nm ×30 nm ×30 nm. The capacitance between Au_{20} and Au(111) is numerically calculated using the COMSOL Multiphysics software, which gives $C_2 = 1.5 \times 10^{-19}$ F. When $C_1 << C_2$, the charging energy is approximately $E_c = e^2/C_2 = 1.1$ eV. Considering a 5% uncertainty for the dimensions, C_2 is in the range between 1.4×10^{-19} F and 1.5×10^{-19} F, resulting the charging energy with an uncertainty of about 0.1 eV.

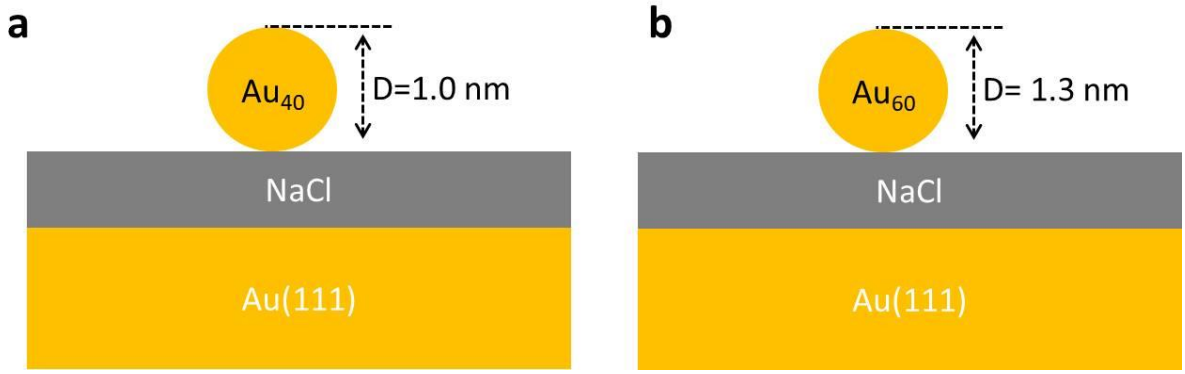

Fig. S4. Electrostatic model to estimate the capacitance of Au_{40}/NaCl/Au(111) and Au_{60}/NaCl/Au(111) systems. Model used for calculation of the capacitance C_2 **a**, between Au_{40} and Au(111), and b, between Au_{60} and Au(111). Both Au_{40} and Au_{60} are modeled as an ideal sphere, with diameter of 1.0 nm and 1.3 nm, respectively. Parameters for NaCl and Au(111) are the same as those used in fig. S3d. Applying similar analysis, the calculated capacitance using COMSOL Multiphysics software for a and b is 1.0×10^{-19} F and 1.4×10^{-19} F, respectively, resulting in charging energies of 1.6 eV and 1.1 eV, respectively. Considering a 5% uncertainty for the dimensions, C_2 for Au_{40} (Au_{60}) is in the range between 1.0×10^{-19} F and 1.1×10^{-19} F (between 1.4×10^{-19} F and 1.7×10^{-19} F), resulting the charging energy between 1.5 eV to 1.6 eV (between 0.9 eV to 1.1 eV).

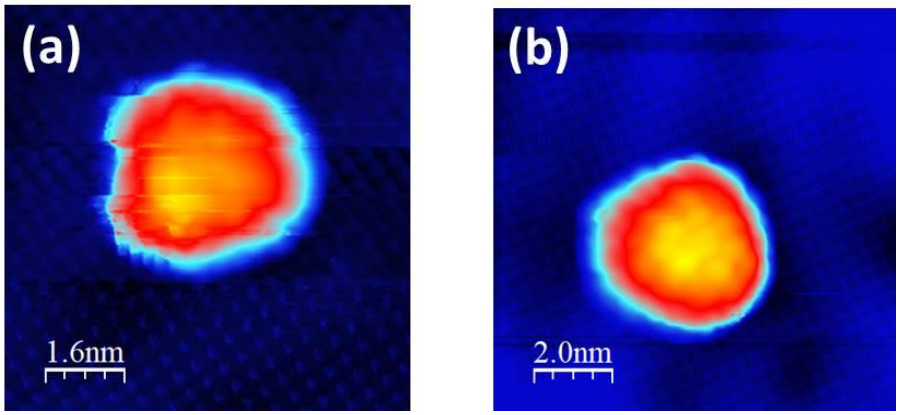

Fig. S5. High-resolution STM images for supported Au_{40} and Au_{60} clusters. Atomic-resolution STM topography image of (a) a Au_{40} agglomerate with height of 1.05 nm (V = –1.8 V, I = 0.5 nA), and (b) a Au_{60} agglomerate with height of 1.4 nm (V = –1.5 V, I = 0.075 nA). Note that in both images there is atomic resolution on NaCl. For the Au_{40} in (a) atoms are not resolved due to an unstable Cl-functionalized tip, while for the Au_{60} in (b) several atoms on the top part of the cluster can be resolved.

Table S1. The relationship between distortion and the HL gap for supported Au_{20}. The HL gaps (in eV) and their relative energies (in eV) of isolated Au_{20} and supported Au_{20} on 3L NaCl/Au(111) with different degrees of distortion from a perfect T_d-symmetry tetrahedral structure. The three supported Au_{20} structures are obtained by optimization of different initial configurations, e.g., Au_{20} on different active sites of NaCl/Au(111) surfaces.

System	Deviation of Au_{20} from T_d symmetry [a] (Å)	Distortion percentage [b] (%)	HL gap (eV)	Relative energy (eV)
Isolated Au_{20}	0	0	1.78	--
Supported Au_{20} (I)	0.03	0.4	1.73	0.04
Supported Au_{20} (II)	0.34	4.3	1.67	0.00
Supported Au_{20} (III)	0.45	5.6	1.51	0.09

[a] It is defined as the largest displacement of an Au atom w.r.t. that with T_d symmetry.
[b] These values are w.r.t. the edge length of 8 Å of Au_{20}.