Supporting information for:

Effects of Oxidation on the Plasmonic Properties of Aluminum Nanoclusters.

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Validation of the Reax Force Field

The Al-O ReaxFF has been proven to qualitatively predict the oxidation kinetics of aluminum slabs and nanoclusters as a function of temperature.^{S1} In order to take the validation one step further, we performed DFT relaxations of small Al_xO_y clusters, and compared the resulting structures and energies with that obtained by the ReaxFF. For comparison of stabilities the formation energy was calculated as

$$E_f = \frac{E(n)_{AlO} - E_{Al} - nE_{O_2}/2}{n}$$
(1)

where $E(n)_{AlO}$ is the energy of an oxide cluster with *n* number of oxygen atoms, E_{Al} the energy of a bare aluminum cluster, and E_{O_2} the energy of an oxygen molecule. Fig. S1 shows the most relevant structures included in the comparison. Previous studies focused on



Figure S1: Formation energy (in eV) of several structures according to DFT and ReaxFF (RFF). Aluminum and oxygen atoms are colored gray and red, respectively. In case in which an icosahedral structure was found, the corresponding atoms are colored yellow, with a central atom colored blue. The larger cluster shown, contains 55 Al atoms. Only the structure corresponding to the ReaxFF energy minimization is shown.

 $Al_{2n}O_{3n}$ structures, ^{S2,S3} Another work studied several small clusters without this stoichiometric restriction, ^{S4} in which the cluster Al_4O_2a was also found to be stable and with the same geometry as the one shown here.

Our study shows that ReaxFF favors the coordination of oxygen with four Al neighbors (inside an aluminum tetrahedron), while for DFT the case of three Al neighbors is energetically more stable (inside an aluminum triangle). Also, the force field tends to overestimate the formation energy. However, the energy discrepancy diminishes as the cluster becomes larger, where quantum effects are less accentuated. The energy difference was found to be larger for random structures than for more symmetric ones. Still, this energy difference is safely within the frames of a qualitative description. Most of the clusters studied contain an icosahedral structure, this geometric feature was reproduced by both, DFT and ReaxFF. After this validation, we conclude that the ReaxFF model correctly estimates the relative energy and structure among nanoclusters.

Fragmentation of AlO nanoclusters

As mentioned in the manuscript, at 1 and 12 atm of O_2 pressure, nanocluster fragmentation is observed, being more evident for the former case. The initial and final configurations of a 561 Al nanocluster at 1 and 12 atm are shown in Fig.S2a-c. The phenomenon is not a consequence of nanocluster fusion, since the system is under a NPT thermostat and the temperature oscillates around 300 K as shown in Fig.S2d. However, local temperature increase could be involved. Why fragmentation is observed in these scenarios but not at high pressure remains an open question. One possibility is that at high pressures, the whole nanocluster surface is attacked by O_2 molecules at unison, while at lower pressure this is done progressively. A complete shell of oxide (former case) could confer more structural stability than a partially formed one (latter case). (c) (d) — 1 atm --- 12 atm 340 Temperature (K) 000 Temperature 280 260 400 0 50 100 200 time (ps) 250 300 350 150

(b)

(a)

Figure S2: (a) Initial configuration of an icosahedral Al_{561} nanocluster. (b,c) Final state of fragmentation at 1 atm (b) and 12 (c) atm of O₂ pressure. (d) Temperature of the systems at 1 and 12 atm as a function of time.

Clusters geometry

In this section the stability of several geometries of Al clusters are studied. Previous studies showed that for noble metal clusters of 13 atoms the buckled biplanar structure (bbp) is even more stable than the icosahedral one (ico).^{S5,S6} Still, the latter remains the most stable for larger clusters. Another well known cluster geometry is the cuboctahedral structure (cub). These three structures were relaxed at the DFT level. Geometries and relative energies are given in Fig. S3. The icosahedral structure is the most stable by far, while the bbp structure



Figure S3: Top and side views of icosahedral (ico), cuboctahedral (cub) and buckled biplanar (bbp) structures for Al_{13} clusters. The energy difference with respect to the most stable structure (ico) according to DFT is also shown.

is the most unstable. Since not even at this size the bbp structure outruns the stability of the icosahedral one, we can safely assume that the latter will also be energetically favorable for larger clusters, which are the focus of our studies.

To be on the safe side, we also evaluated the energetics of icosahedral and cuboctahedral structures at the ReaxFF level. Fig. S4 shows the energy per atom as a function of several Al cluster sizes. Also in this case the icosahedral geometry is the most stable one. We therefore



Figure S4: Energy per atom of icosahedral (ico) and cuboctahedral (cub) structures for Al clusters of several sizes.

focus our study on this structure.

References

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