Supplementary Information

Breakdown of the correlation between oxidation states and core electron binding energies at the sub-nanoscale

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Supplementary Figures

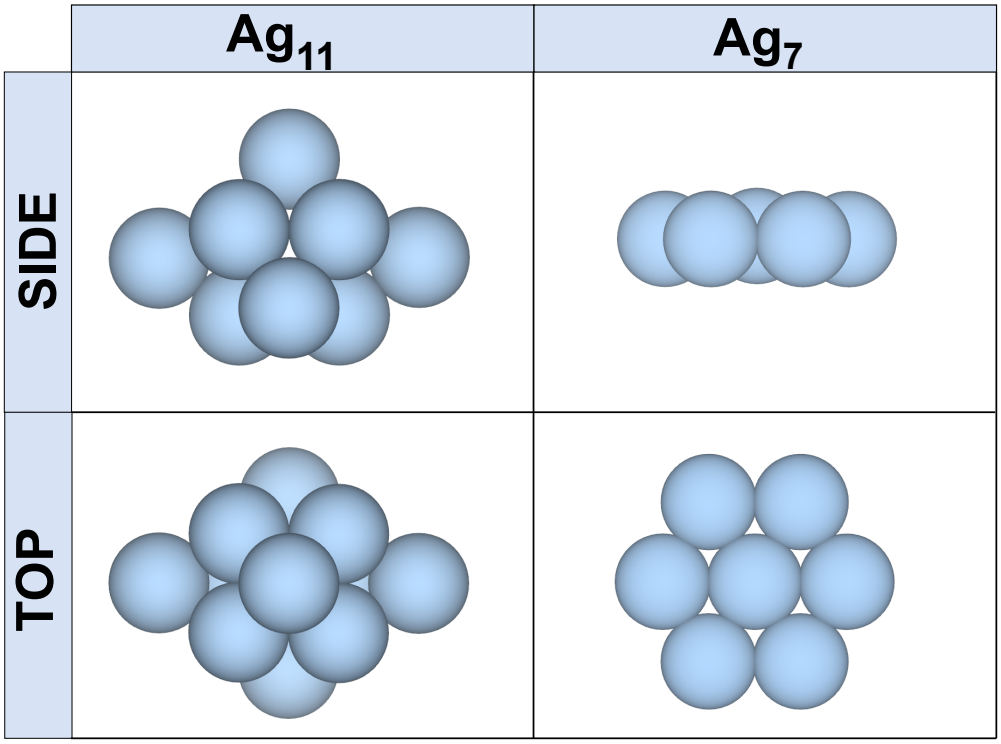

Figure S1: Gas-phase Ag_n^+ cluster morphology. Side and top views of the DFT calculated minimum energy morphology of Ag_{11}^+ and Ag_7^+ clusters in the gas-phase.

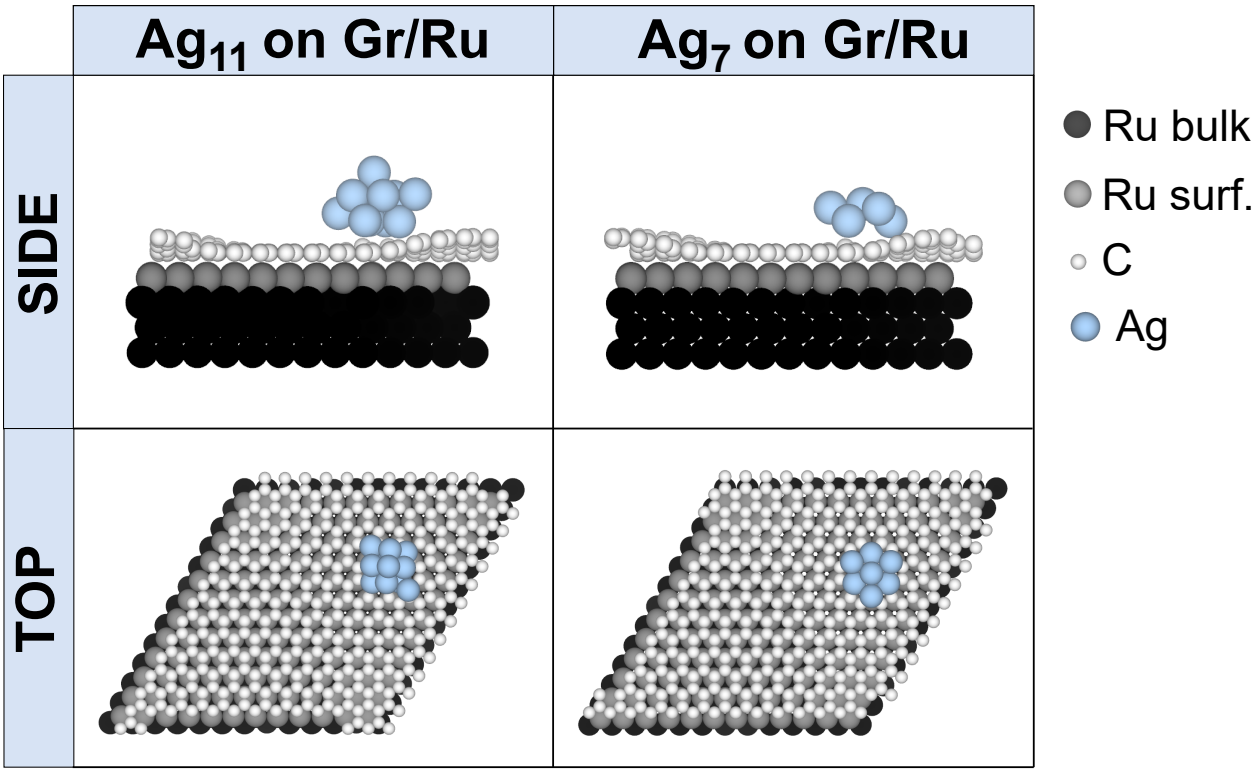

Figure S2: Gr/Ru moiré cell for DFT calculations. Side and top views of the Gr/Ru moiré cell used for the DFT calculations for the Ag_{11} and Ag_7 clusters. The super-cell is composed of 4 12×12 layers of Ru and by a 13×13 graphene single layer, which correspond to a complete moiré unit cell.

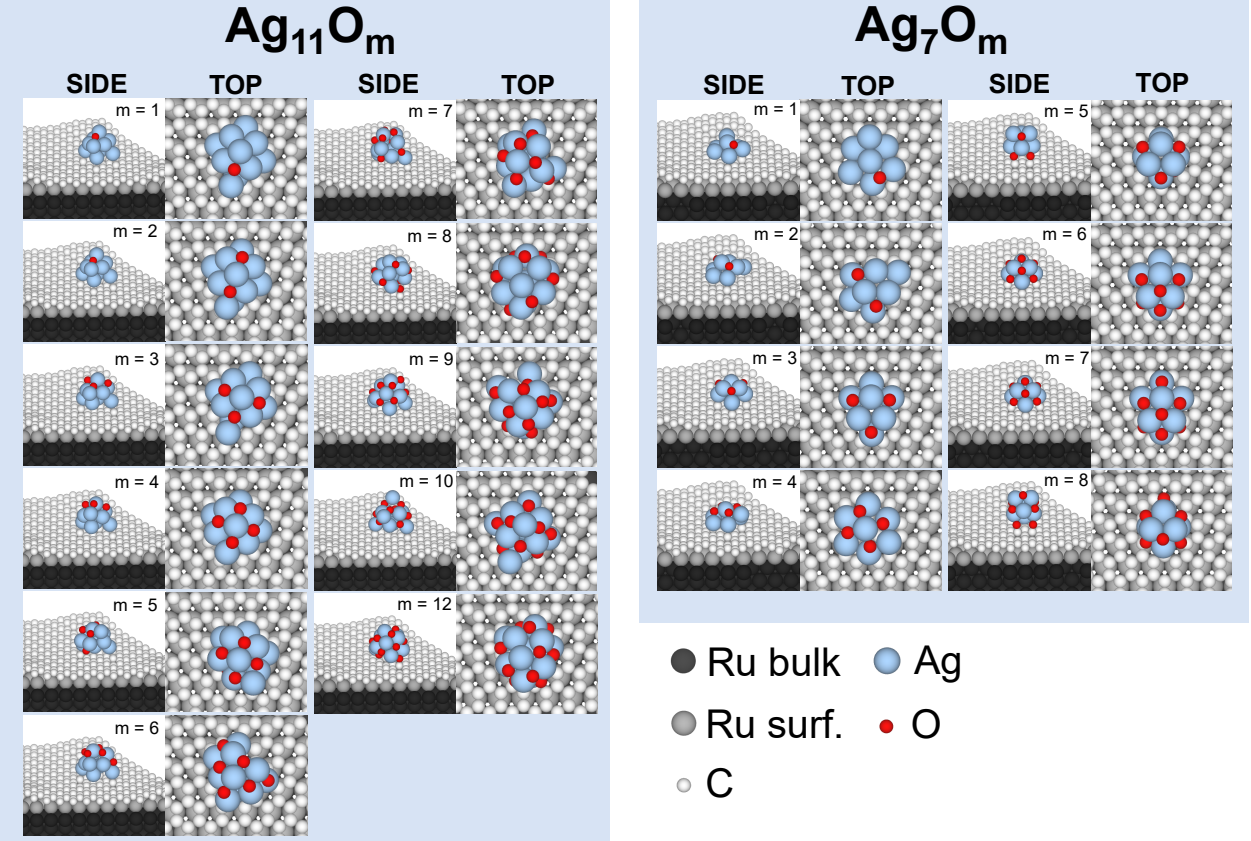

Figure S3: Minimum energy relaxed structures of oxidized clusters. Side and top views of DFT calculated minimum energy relaxed structures for the oxidized Ag_{11} and Ag_7 clusters supported on Gr/Ru.

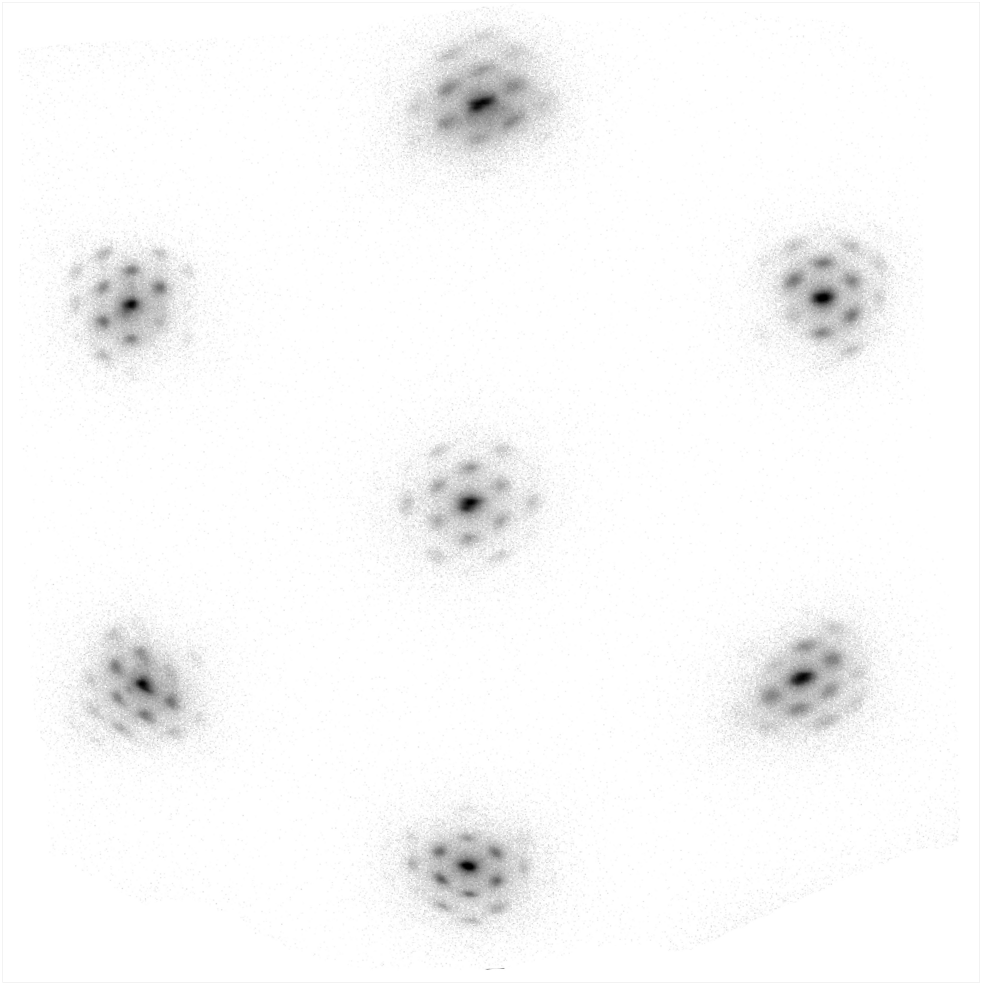

Figure S4: Graphene characterization. Spot profile analysis low energy electron diffraction pattern of the Gr/Ru surface acquired with electron energy E = 158 eV showing the moiré-induced diffraction spots.

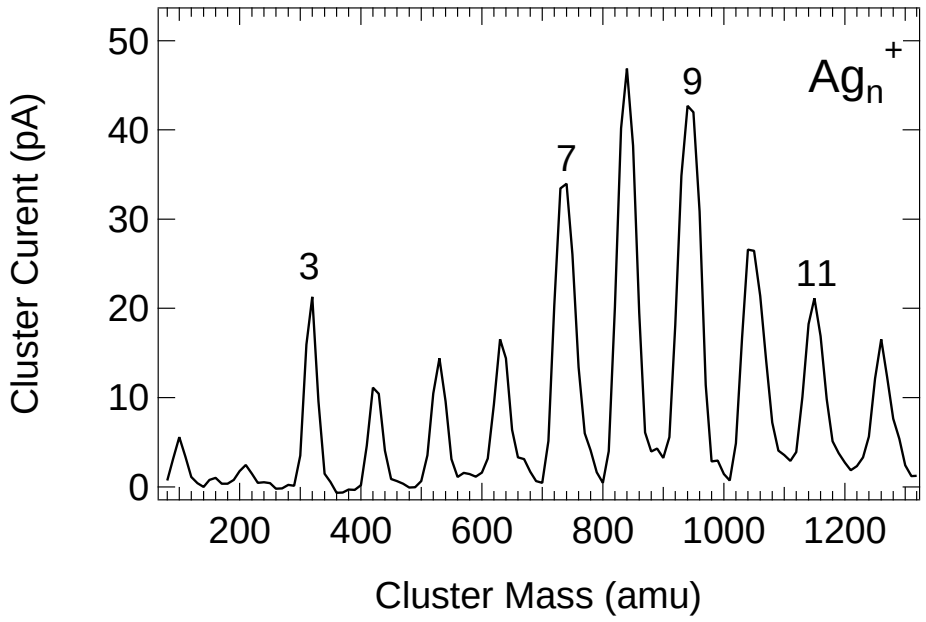

Figure S5: Mass spectrum of size selected Ag_n^+ clusters obtained with the ENAC cluster source for n = 1 - 12.

Supplementary Discussion

Resolution to different cluster conformations

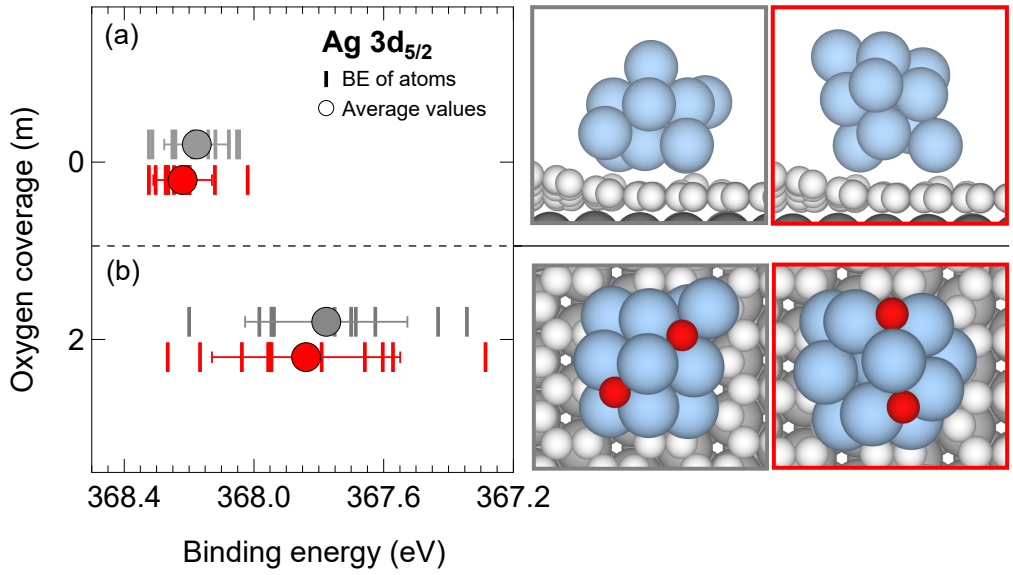

Figure S6: (a) DFT-calculated core electron binding energies for clean Ag_{11} clusters in two different adsorption configurations (reported on the right-hand side of the figure). The average value of the BE is reported as filled dot, while the standard deviation of the BE distribution is reported as error bars of the average value. (b) same as in (a), but for two different configurations of $Ag_{11}O_2$ with two O atoms in different adsorption sites.

An interesting issue to evaluate is the dependency on the different cluster configuration of the core electron binding energy for a few selected configurations of our size-selected graphene-supported clusters. In order to do so, we have carried out additional DFT-based calculations considering clean Ag_{11} clusters with different adsorption configuration on graphene. In addition to them, we have considered $Ag_{11}O_2$ clusters for which we have varied the adsorption site of the two O atoms. The results for clean and the oxygen covered clusters are reported in Figure S6.

It was found by calculations that for Ag_{11} different adsorption configurations (as the two shown in the Figure S6a) will lead, as expected, to different binding energy distributions for the core levels. However, the difference in the average binding energy value (40 meV) is much smaller than the standard deviation of the distribution of the same binding energies, which amounts to 100 and

90 meV for the two different configurations, respectively. In the same way, similar calculations considering Ag_{11} with two oxygen atoms adsorbed on different sites on the cluster have shown that the distribution of the binding energy is slightly different according to the different adsorption site. However, also in this case, the differences between the average binding energy in the two different configurations (60 meV) is much smaller than the associated standard deviations of the binding energy distributions, which amounts to 250 and 290 meV for the case of two O atoms adsorbed.