Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Oxidation at the sub-nanoscale: oxygen adsorption on graphene-supported size-selected Ag clusters.

Electronic Supplementary Information.

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SUPPORTING FIGURES S1-S6

LEED diffraction pattern of the graphene/Ru(0001) moiré lattice

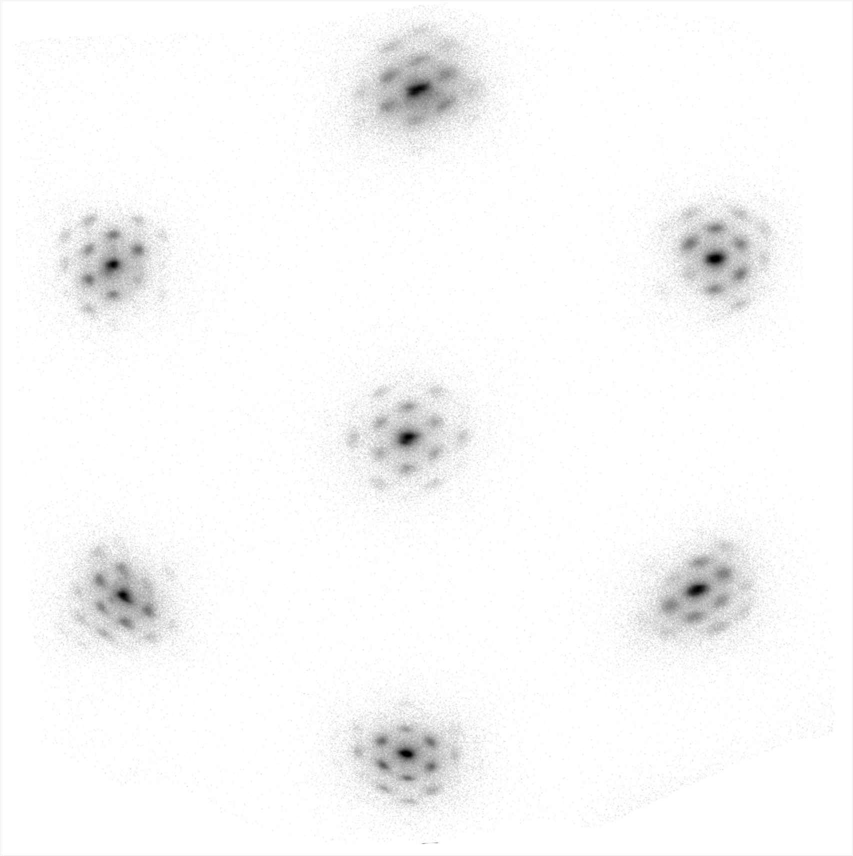

Fig. S1. Spot profile analysis low energy electron diffraction pattern of the GR/Ru surface aquired with electron energy E = 158 eV showing the moiré-induced diffraction spots.

Mass spectrum of mass-selected Ag_n^+ clusters

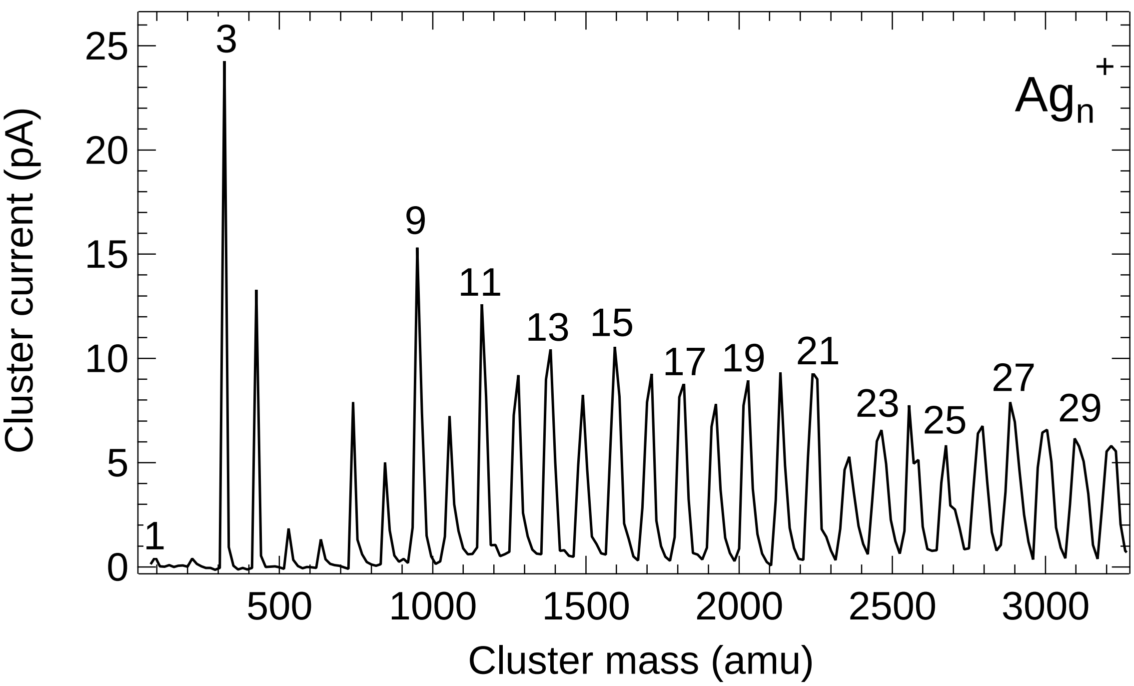

Fig. S2. Mass spectrum of size-selected Ag_n^+ clusters produced with ENAC. The mass selection is performed with a Extrel Quadrupole Mass Spectrometer in the range 100 - 3300 amu and allows to select the Ag_n^+ clusters with atomic precision for n = 1 - 30.

O_2 dissociation induced by soft X-rays at 20 K

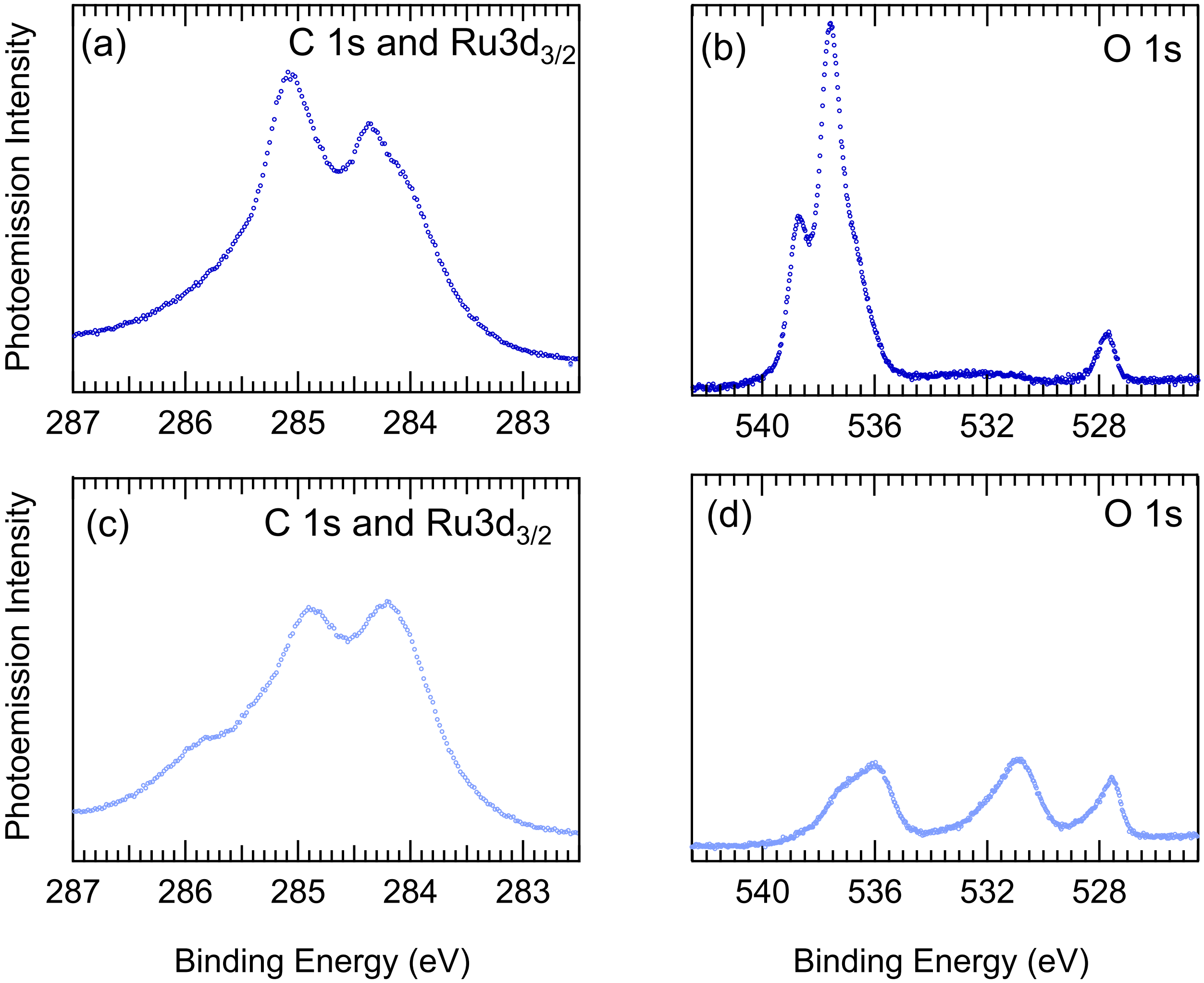

Fig. S3. High-resolution X-ray photoelectron spectroscopy of the C 1s (and Ru $3d_{3/2}$) and O 1s of the Gr/Ru sample with Ag_{11} clusters exposed to 0.5 L of O_2 at 20K before (a and b) and after (c and d) the dissociation of physisorbed O_2 induced exposing the sample to soft X-rays. The presence of molecular physisorbed O_2 can be detected through its characteristic double-component spectrum (core level shift of about 1.12 eV) typically measured for gas phase O_2. Such lineshape is altered after the exposure to soft X-rays and is replaced by several new components which can tentatively be associated to oxygen on graphene defects, enolate and epoxy species.

Oxygen exposure of clusters on Gr/Ru at 70 K

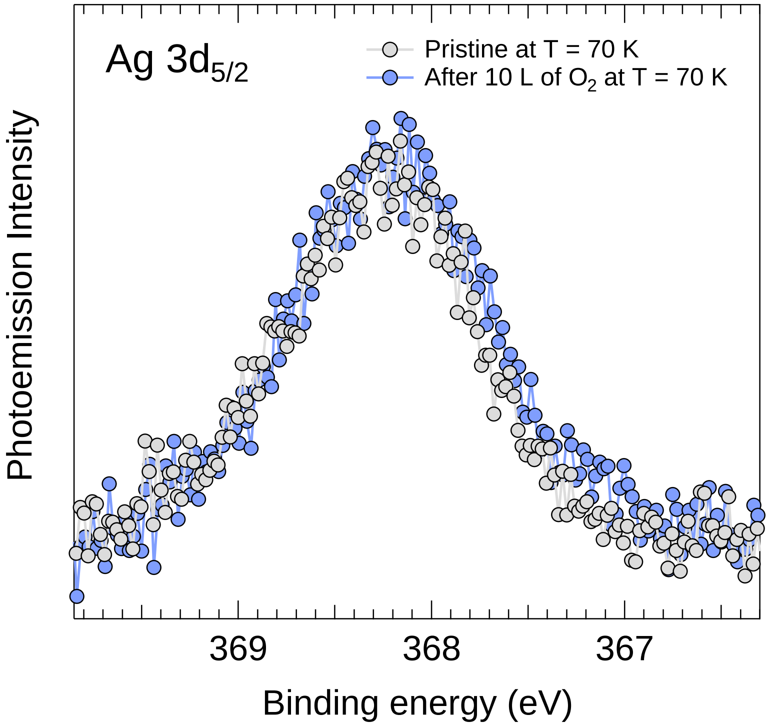

Fig. S4. High resolution X-ray photoelectron spectroscopy of the Ag $3d_{5/2}$ core level of the Ag_{11} cluster at 70 K before (gray) and after (light blue) an exposure to 10 L of O_2.

Optimized geometry for $Ag_{11}O_{2m}$ clusters for m = 0 - 6

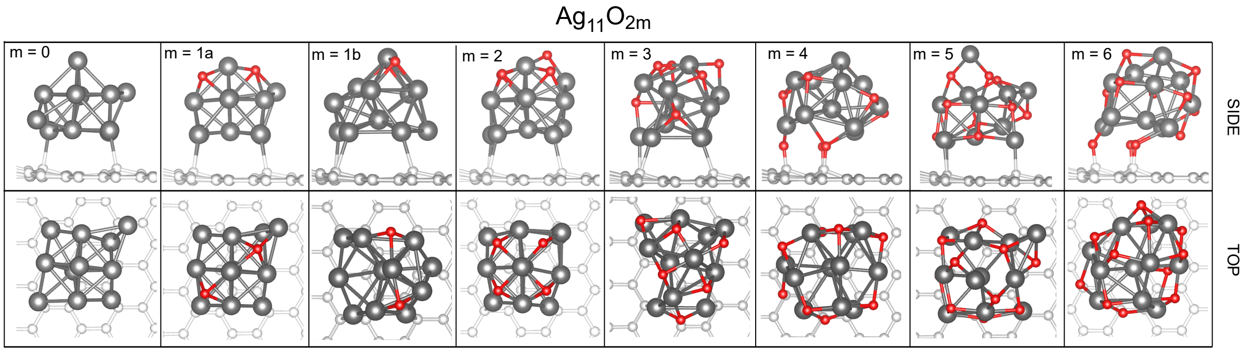

Fig. S5. Side and top views of the optimized geometry of $Ag_{11}O_{2m}$ nanoclusters obtained by DFT calculations, for an increasing amount of oxygen ($m = 0 - 6$). Ag and O are shown in dark grey and red, respectively. We performed calculations on the $Ag_{11}O_2$ structure starting both with oxygen on symmetric three-fold sites ($m = 1a$) and on adjacent sites ($m = 1b$) and in both cases we obtained the linear O–Ag–O motif typical of d^{10} Ag(I) ions. The Ru atoms were hidden to provide a clearer view on the clusters, but were included in the global cell for the DFT calculations.

Structural comparison of Ag$_{11}$ in gas phase and deposited on Gr/Ru.

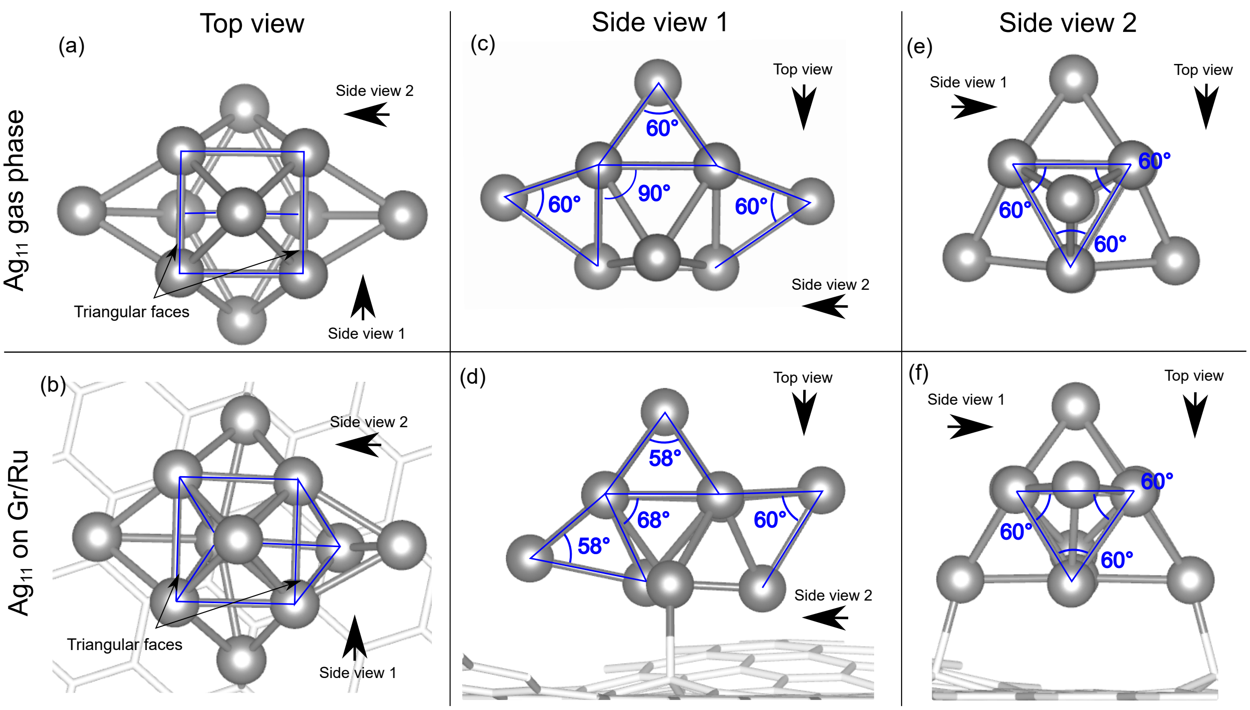

Fig. S6. (a) Top view of the Ag$_{11}$ cluster in gas phase with the triangular prism core highlighted in blue. (b) The core is modified after the deposition as it evolves from (c) a right triangular prism in the gas phase to (d) an oblique triangular prism with an angle of 68°. The Ag atoms capping the faces of the prism follow this modification and maintain their geometry with respect to prismatic core (c-f). The Ru and C atoms were hidden to provide a clearer view on the clusters.