

Table S1. Representative Ag clusters from the (110) surface upon four electron irradiation doses (0.125, 0.250, 0.500 and 1.000 e⁻). Ag-Ag distances (Å) and the related ρ (a.u.) and $\nabla^2\rho$ (a.u.) are compared to Ag-Ag bonding in Ag bulk.

| System | $d_{\text{Ag-Ag}}$ | ρ | $\nabla^2\rho$ |
|----------------------------------|--------------------|--------|----------------|
| Cluster 1 – 0.125 e ⁻ | 2.845 | 0.230 | 1.572 |
| | 2.744 | 0.274 | 2.346 |
| | 2.845 | 0.230 | 1.572 |
| | 2.744 | 0.274 | 2.346 |
| Cluster 2 – 0.250 e ⁻ | 2.710 | 0.310 | 2.242 |
| | 2.869 | 0.233 | 1.510 |
| | 2.859 | 0.234 | 1.574 |
| | 2.882 | 0.209 | 1.579 |
| Cluster 3 – 0.500 e ⁻ | 2.702 | 0.308 | 2.470 |
| | 2.842 | 0.224 | 1.820 |
| Cluster 4 – 1.000 e ⁻ | 2.837 | 0.242 | 1.719 |
| | 2.822 | 0.264 | 1.454 |
| | 2.739 | 0.283 | 2.351 |
| Metallic Ag | 2.880 | 0.218 | 1.592 |

Table S2. Representative O₂ molecules formed in (100) and (111) surfaces upon two electron irradiation doses (0.125 and 0.250 e⁻). O-O distances (Å) and the related ρ (a.u.) and $\nabla^2\rho$ (a.u.) are compared to O-O bonding in O₂ gas phase.

| System | $d_{\text{O-O}}$ | ρ | $\nabla^2\rho$ |
|------------------------------|------------------|--------|----------------|
| (100) - 0.125 e ⁻ | 1.380 | 2.308 | -7.575 |
| (111) - 0.250 e ⁻ | 1.541 | 2.659 | -12.124 |
| Molecular O ₂ | 1.234 | 3.435 | -23.764 |

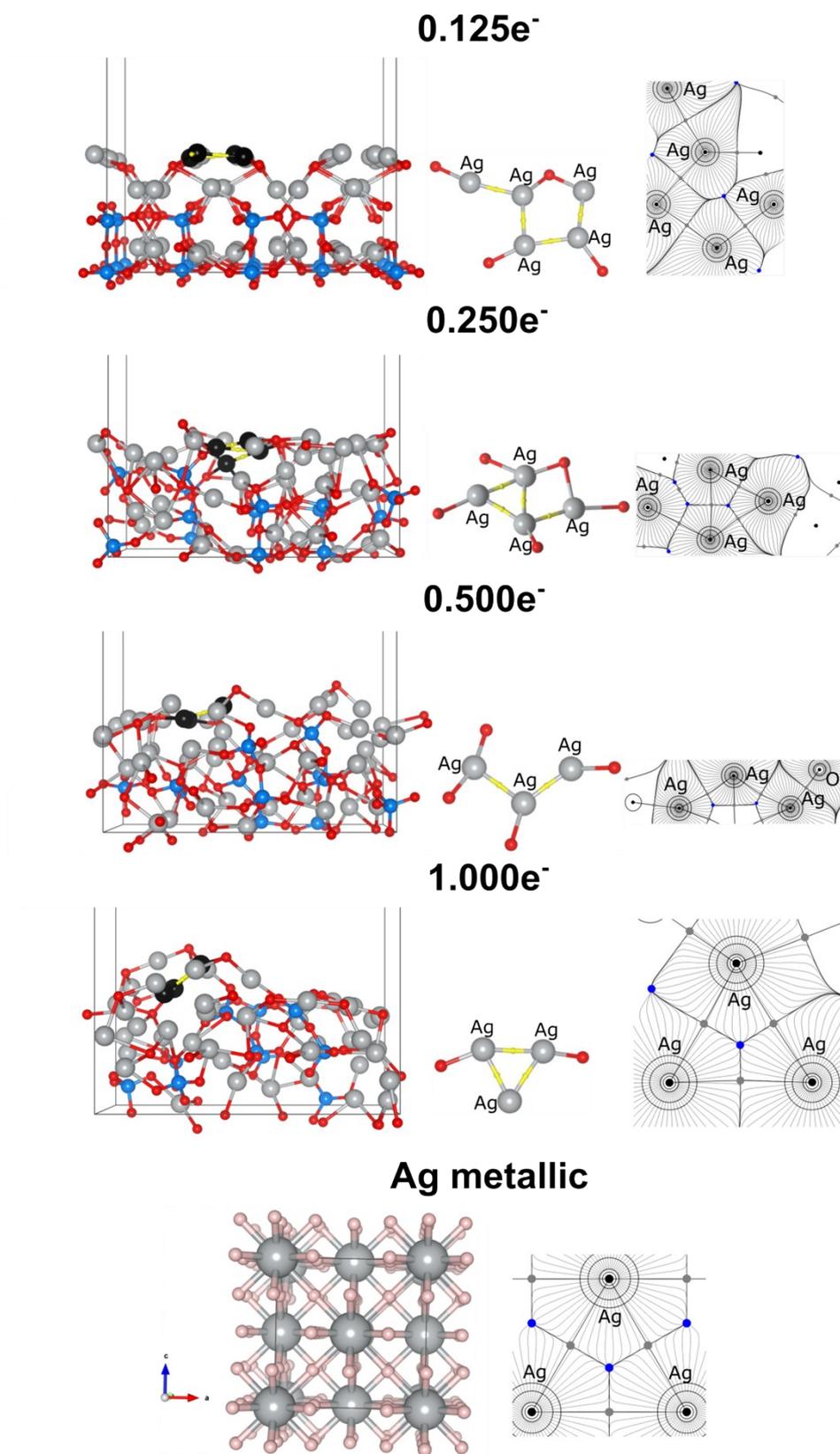


Figure S1. Representative Ag clusters from the (110) surface upon four electron irradiation doses (0.125, 0.250, 0.500 and 1.000 e⁻). Left panels: system lateral views, where Ag, P and O atoms are coloured in grey, blue and red, respectively. The Ag atoms in the selected cluster are in black. Middle panels: top views of the selected Ag clusters. Right panels: illustrative representations of the bonding critical points (BCPs) of the selected Ag clusters.

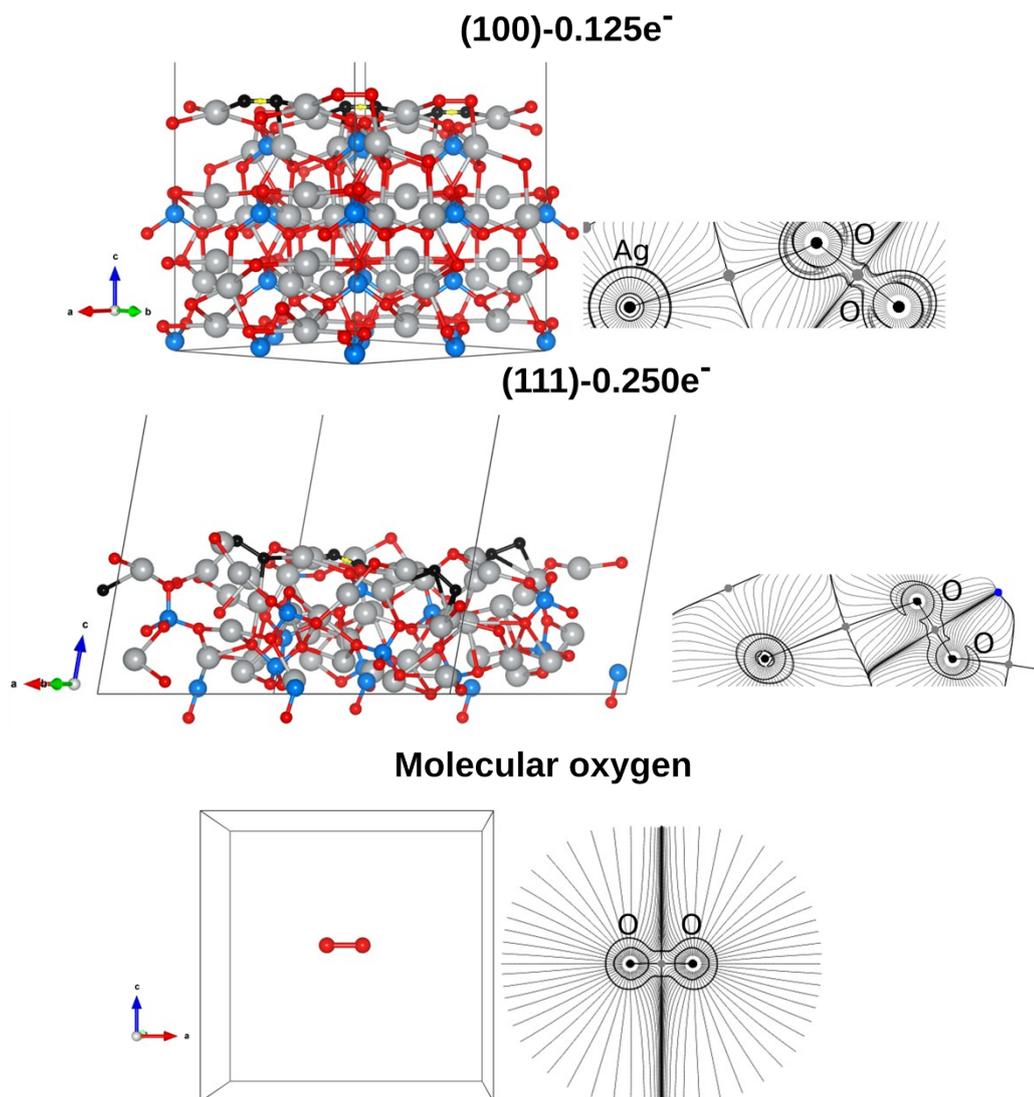


Figure S2. Representative O₂ molecules formed in (100) and (111) surfaces upon two electron irradiation doses (0.125 and 0.250 e⁻). Left panels: system lateral views, where Ag, P and O atoms are coloured in grey, blue and red, respectively. The O atoms in the formed O₂ molecules are in black. Right panels: illustrative representations of the bonding critical points (BCPs) of the selected formed O₂ molecules.