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Self-seeded nucleation of Cu nanoclusters on $Al_2O_3/Ni_3Al(111)$: an ab-initio investigation

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Fig. S1 shows the rearrangement of the electron density for the configurations with the smallest Cu seeds in the hole of $Al_2O_3/Ni_3Al(111)$. In any case there is a remarkable electron accumulation between the Cu atoms at the bottom of the defect and the metallic alloy beneath, indicating the formation of rather strong covalent bonds. It is also interesting to notice other regions of electron accumulation in different configurations: in the case of 2-Cu atoms (i), around the second Cu atom in the hole and the lateral Al and O ions of the defect; in both cases of 2-Cu and 3-Cu atoms (ii), around the dimer at the bottom of the hole and again the lateral Al and O ions; in the case of 3-Cu atoms (i), between the second and third Cu atom of the seed, indicating a strong bond between them rather than between the first and the second. This indication is also confirmed by the comparison of interatomic distances, reported in Table S1.

Fig. S2 shows the rearrangement of the electron density for a Cu dimer adsorbed on top of an oxygen atom of alumina. In panel a), the difference between the charge density of the entire system and the one of the substrate plus the one of the Cu dimer separately is shown. When compared with Fig. S1 for the case of 2-Cu atoms (i), obtained in a similar way, it qualitatively suggests that the bond of the dimer with the oxide surface is weaker than the one with the metallic alloy, as it is indeed indicated by the calculated adsorption energies (-0.96 eV and -1.86 eV, respectively). In panel (b) the charge density difference, calculated extracting to the density of the entire system the ones of the substrate with one adsorbed Cu atom plus the one of the second Cu separately, shows the very strong bond within the Cu pair, whereas no relevant change is observed in the bonding of the lowest Cu atom with the oxide surface: this is also confirmed by the calculated adsorption energies that gives -0.97 for a single Cu atom adsorbed on top of a surface oxygen (T_1 site in Table 1), very similar to the value of -0.96 eV for the entire dimer.

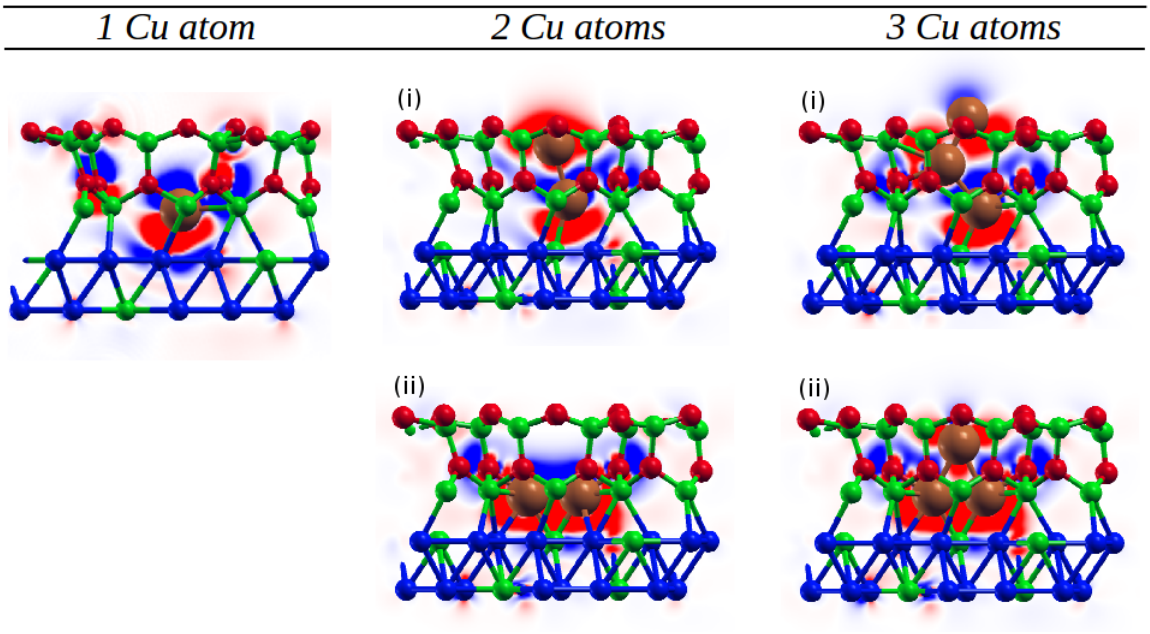

Figure S1: Side view of the equilibrium configurations for Cu seeds on alumina/$Ni_3Al(111)$ composed of up to three atoms, and electron charge density difference plots, calculated extracting to the density of the entire system the ones of the bare substrate and the Cu seeds calculated separately. The plain containing the Cu atoms is shown. Red balls, O atoms; green, Al; blue, Ni; brown, Cu. Red areas in the charge density difference plots indicate electronic density accumulation; blue color, depletion

seed	distances (Å)	seed	distances (Å)	seed	distances (Å)
1	Al-Cu_1 = 2.25		Al-Cu_1 = 2.27		Al-Cu_1 = 2.28
$2^{(i)}$	Al-Cu_1 = 2.39		Al-Cu_2 = 2.28		Al-Cu_2 = 2.29
	Cu_1-Cu_2 = 2.49		Cu_1-Cu_2 = 2.28		Cu_1-Cu_2 = 2.24
$2^{(ii)}$	Al-Cu_1 = 2.27	$4^{(ii)}$	Cu_1-Cu_3 = 2.48	$5^{(ii)}$	Cu_1-Cu_3 = 2.53
	Al-Cu_2 = 2.28		Cu_2-Cu_3 = 2.47		Cu_2-Cu_3 = 2.52
	Cu_1-Cu_2 = 2.26		Cu_3-Cu_4 = 2.17		Cu_3-Cu_4 = 2.43
$3^{(i)}$	Al-Cu_1 = 2.25		Cu_1-Cu_4 = 2.47		Cu_3-Cu_5 = 2.43
	Cu_1-Cu_2 = 2.45		Cu_2-Cu_4 = 2.47		Cu_4-Cu_5 = 2.29
	Cu_2-Cu_3 = 2.27		Al-Cu_1 = 2.23		Al-Cu_1 = 2.27
$3^{(ii)}$	Al-Cu_1 = 2.35		Al-Cu_2 = 2.23		Al-Cu_2 = 2.27
	Al-Cu_2 = 2.34		Cu_1-Cu_2 = 2.28		Cu_1-Cu_2 = 2.27
	Cu_1-Cu_2 = 2.23		Cu_1-Cu_3 = 2.50		Cu_1-Cu_3 = 2.56
	Cu_1-Cu_3 = 2.48	$5^{(i)}$	Cu_2-Cu_3 = 2.49		Cu_2-Cu_3 = 2.46
	Cu_2-Cu_3 = 2.49		Cu_3-Cu_4 = 2.18		Cu_3-Cu_4 = 2.14
$4^{(i)}$	Al-Cu_1 = 2.26		Cu_1-Cu_4 = 2.51	6	Cu_1-Cu_4 = 2.49
	Al-Cu_2 = 2.27		Cu_2-Cu_4 = 2.51		Cu_2-Cu_4 = 2.58
	Cu_1-Cu_2 = 2.26		Cu_3-Cu_5 = 2.37		Cu_3-Cu_5 = 2.53
	Cu_1-Cu_3 = 2.47		Cu_4-Cu_5 = 2.36		Cu_4-Cu_5 = 2.78
	Cu_2-Cu_3 = 2.47				Cu_5-Cu_6 = 2.23
	Cu_3-Cu_4 = 2.26				Cu_3-Cu_6 = 2.86
					Cu_4-Cu_6 = 2.53

Table S1: Interatomic distances for the seeds shown in Figure 4

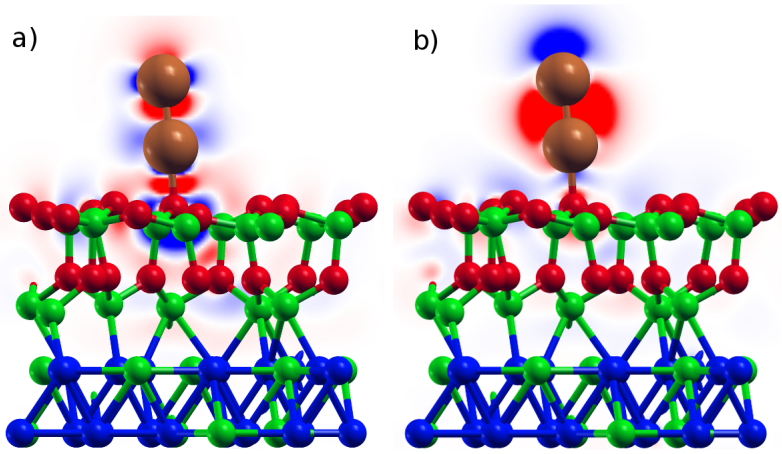

Figure S2: Side view of the equilibrium configurations for a Cu dimer on alumina/$Ni_3Al(111)$, and electron charge density difference plots, calculated extracting to the density of the entire system the ones of a) the bare substrate and the Cu dimer separately calculated and b) the substrate with one Cu ad-atom adsorbed and a Cu atom separately calculated. A plane containing the Cu atoms is shown. Red balls, O atoms; green, Al; blue, Ni; brown, Cu. Red areas in the charge density difference plots indicate electronic density accumulation; blue color, depletion