Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information for Spontaneous doping of two-dimensional NaCl films with Cr atoms: aggregation and electronic structure

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Experiment

Figure S1(a) shows the coexistence of 1L and 2L NaCl. The 2L NaCl island has a pronounced square shape with perfectly straight edges, while the 1L NaCl islands have a somewhat rounded shape with more random edges.

Upon deposition of Cr dopant atoms [Fig. S1(b)], the influence on the NaCl island thickness and morphology includes a change of shape towards truncated square islands and the disappearance of 1L islands.

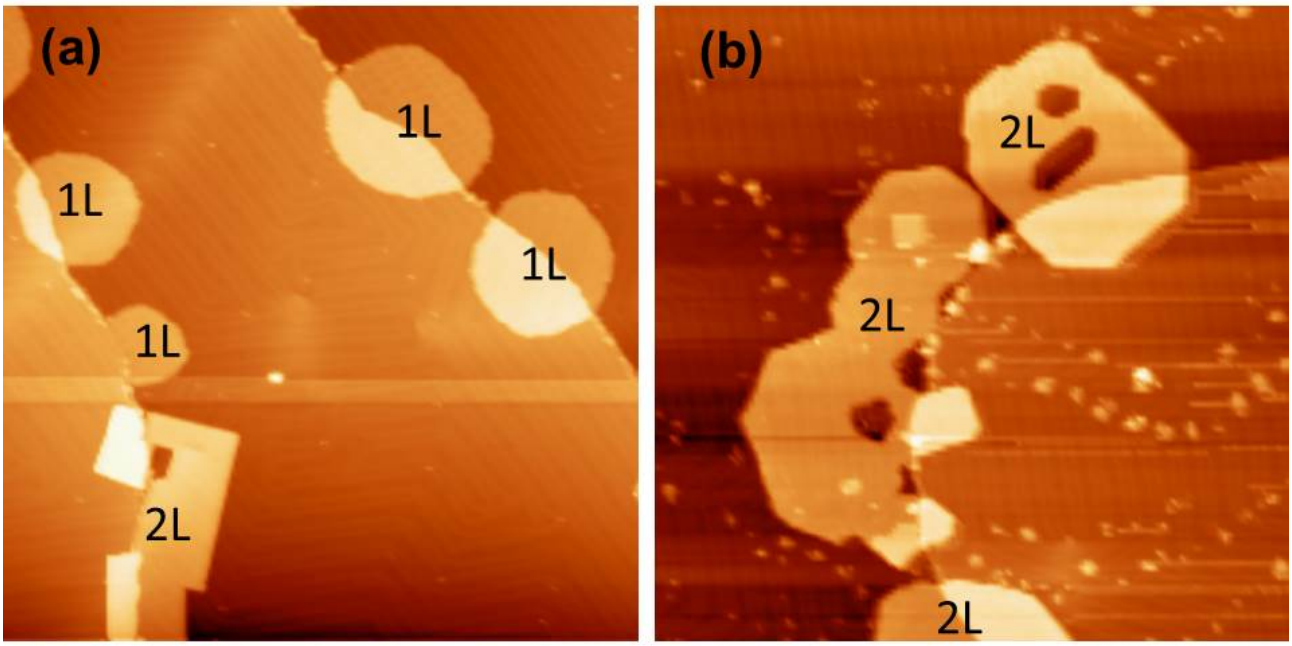

Figure S1 – (a) 156×156 nm^2 STM topography images of bare 1L and 2L NaCl islands on Au(111). (b) 156×156 nm^2 STM topography images after Cr deposition. All 1L NaCl islands have converted into 2L NaCl islands.

Figure S2 demonstrates the statistical analysis of the distribution of Cr dopants (Cr_{Cl}) in the Cr-rich 2L NaCl region. Figure S2(a) shows a STM topography close-up view of a Cr-rich region on which we applied Delaunay triangulation (DT). A DT-based histogram of the nearest neighbour distances *d* between the Cr dopants is plotted in Fig. S2(c). The distance histogram can be fitted by a Gaussian line providing a most likely nearest neighbour distance of 1.2 nm ±0.2 nm [see inset in Fig. S2(c)], which indicates that there is a short-range order for the Cr distribution.

A fast Fourier transform (FFT) image of Fig. S2(a) is presented in Fig. S2(b). The two sets of diffraction spots in the FFT image originate from the long-range order of the Au(111) herringbone structure (indicated by the black arrow) and from the periodic Moiré structure (indicated by the white arrow) that arises due to the mismatch between the square NaCl atomic lattice and the hexagonal Au(111) atomic lattice. Besides the diffraction spots, the FFT also reveals a halo pattern that originates from the distribution of the Cr atoms, implying an amorphous structure of Cr dopants.[1]

Both the statistical distribution of the Cr dopants and the halo pattern in the FFT image indicate that the Cr dopants in the Cr-rich region result in short-range order, and the formation of an amorphous phase.

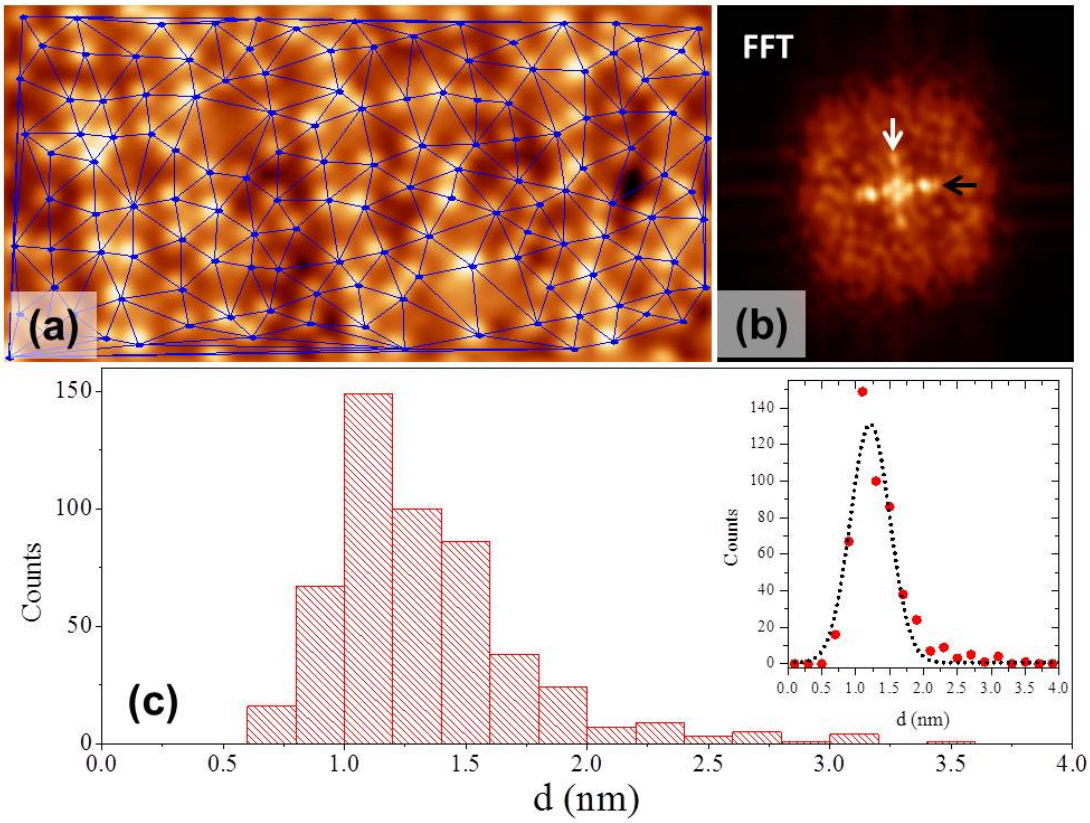

Figure S2 – (a) 20×10 nm^2 STM topography image of a Cr-rich region on 2L NaCl/Au(111). The superposed triangular grid is obtained using the Delaunay triangulation method. (b) 4 nm^{-1}×4 nm^{-1} FFT pattern of (a). (c) Histogram of the nearest-neighbour distances of the Cr dopants in (a). The width of the bins is 0.2 nm. Inset: Gaussian fitting of (c).

Theory

Figure S3 reports the density of states for Cr atoms replacing Na and Cl in unsupported NaCl 2L films:

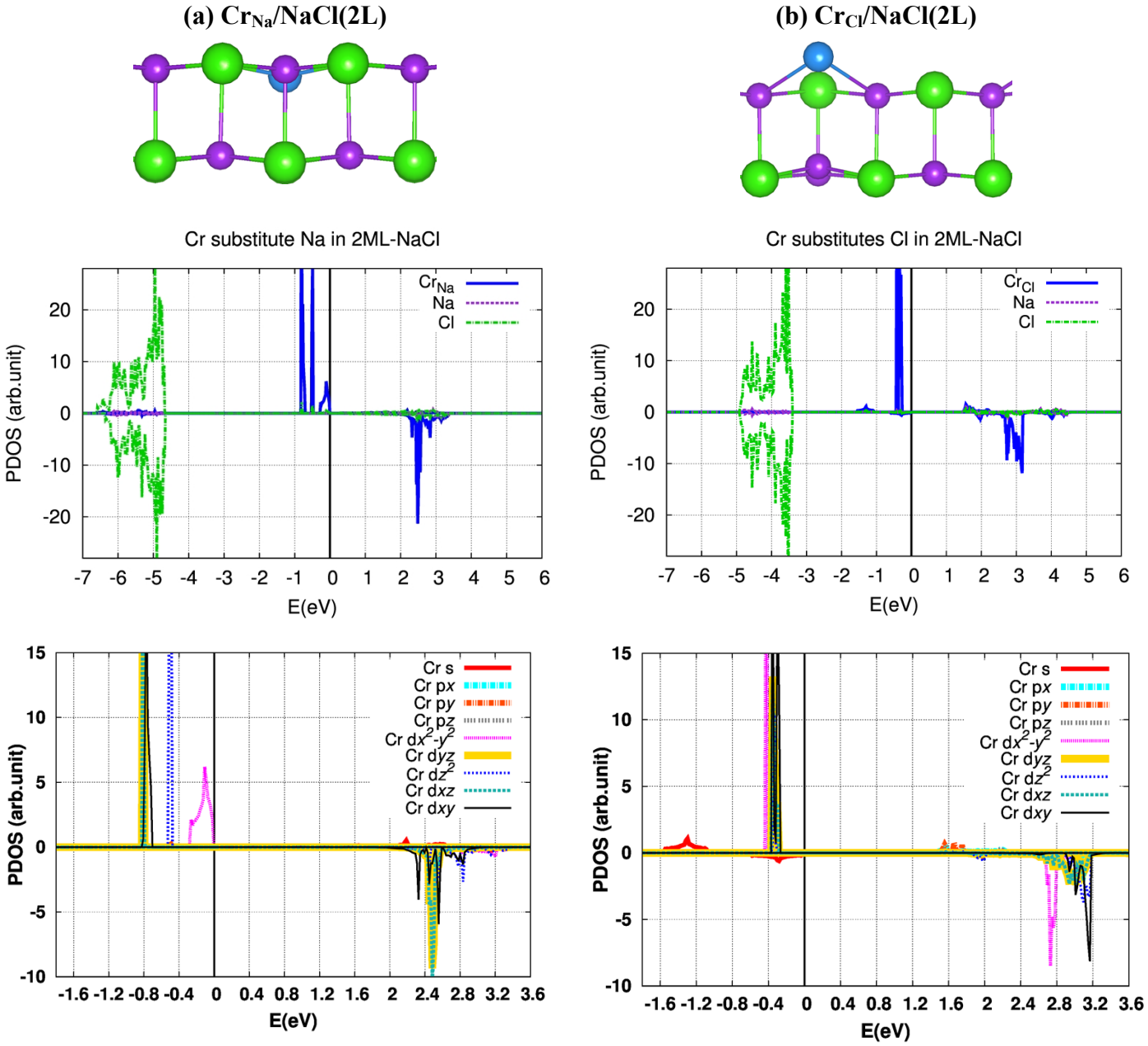

Figure S3 – Structure (top, side view) and projected density of states (PDOS, bottom) of unsupported NaCl 2L films with Cr substituting Na (a) and Cl (b) (12.5% Cr doping). Decomposition of Cr 3*d* orbitals and 4*sp* orbitals is presented in the bottom panel. Zero energy corresponds to the highest occupied state.

Figure S4 (a) shows the PDOS curves of Cr 3*d* orbitals and 4*sp* orbitals in Cr_{Na} in supported NaCl 2L films. The PDOS curve of the four Cl atoms closest to the Cr atom is plotted in Fig. S4 (b). When comparing Figs. S4 (a) and (b), three peaks are observed at 1.8, 2.2 and 2.4 eV, indicating that Cl 3*p* orbitals hybridize with the Cr $3d_{xy}$ (at 1.8 eV), $3d_{xz}$+$3d_{yz}$ (at 2.2 eV) and especially $3d_{x^2-y^2}$ (at 2.4 eV).

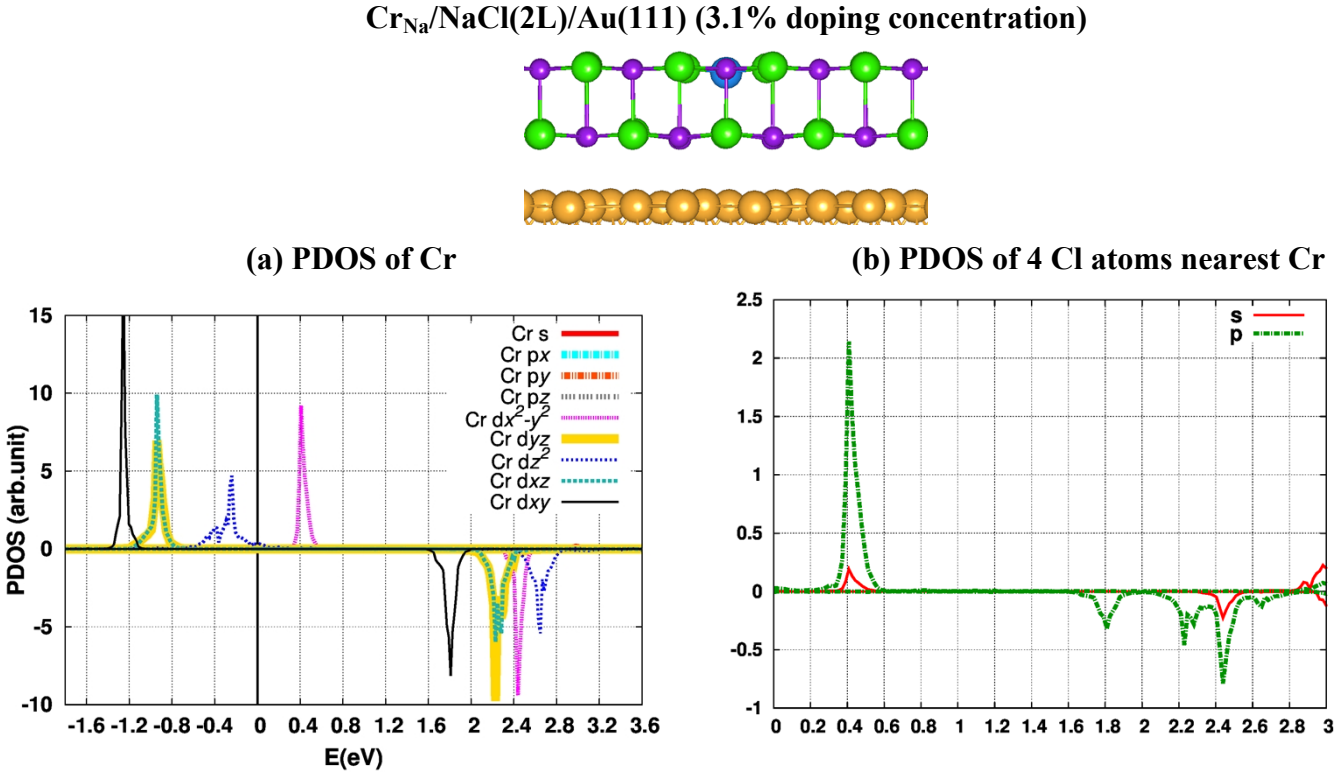

Figure S4 – Structure and projected density of states (PDOS) of Cr_{Na} NaCl(2L)/Au (111). (a) Cr 3*d* orbitals; (b) 3*s* and 3*p* orbitals of the four Cl nearest neighbors to Cr (3.1% Cr doping).

Figure S5 shows the structure and the DOS curves for Cr_{Cl} in supported NaCl 2L films comparing two different situations: (a) the Cr atom is forced to be in the top NaCl layer, and (b) the Cr atom is protruding from the surface [case (b) is by 0.3 eV more stable than case (a)].

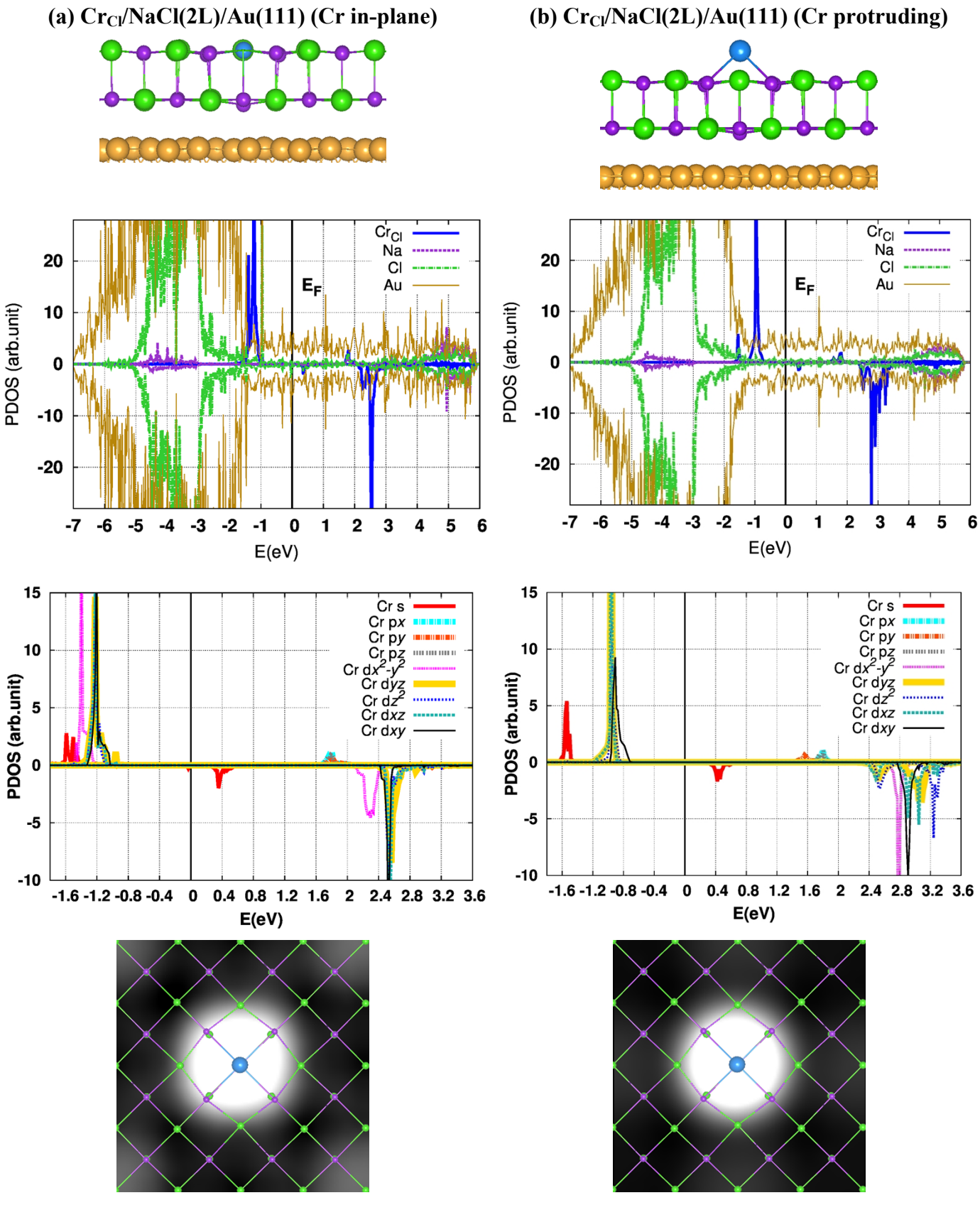

Figure S5 – Structures, projected density of states (PDOS) and simulated STM topography images of NaCl(2L)/Au(111) of Cr substituting Cl (3.1% Cr doping) with Cr staying in the surface layer (a) and Cr protruding from the surface (more stable) (b) (Decomposition of Cr 3*d* orbitals and 4*sp* orbitals is also shown).

Reference

1. Z. Huang, H. Li, Z. Pan, Q. Wei, Y. J. Chao and X. Li, *Scientific reports*, 2011, **1**, 148.