Atomic-resolution spectroscopic imaging in a new generation of electron microscopes is now capable of unravelling bonding details at buried interfaces and clusters, providing both physical and electronic structure information [1]. In some cases the sensitivity and resolution extends to imaging single dopant atoms or vacancies in their native environments. The thousand-fold increase in electron energy loss spectroscopy (EELS) mapping speeds over conventional microscopes allows us to collect data from millions of spectra, generating statistically meaningful maps of heterogeneous populations – such as the facet-dependent leaching in fuel-cell catalysts nanoparticles. In addition, transition radiation generated by the relativistic electron microscope beam also allows the optical modes of photonic structures to be mapped at nanometer resolution. The detection and control of interface defects using EELS, closely-coupled with atomically-precise growth methods, has enabled the realization of interface-stabilized states unreachable in their bulk counterparts, including an oxidation-resistant 2D metal [2]; a 2D superconductor between two band insulators [3]; and, by eliminating extended 2D defects, ferromagnetic tunnel junctions a few unit cells thick.