A Next Significant Innovation in APPES: Probing the Valence Band Electronic Structure with Low Kinetic Energy Electrons with He I/II Photons at Near Ambient Pressures in a Lab-APPES

Electron Spectroscopy for Chemical Analysis (ESCA) works on photoelectric effect; by illuminating UV or x-ray photons, electrons are ejected from the various atomic or molecular orbitals. Electrons that are ejected into the vacuum should reach the detector, without undergoing any collision (or inelastic scattering) with any other atoms within the solid or any gas molecules in vacuum; due to this stringent requirement ultra high vacuum (UHV – less than 10-9 mbar) is maintained in ESCA. Recent advancements in electronics and mechanical designs made possible to measure ESCA around near ambient pressures (NAP) (~1 mbar) with x-ray and synchrotron radiation. This is also popularly known as Ambient Pressure PhotoElectron Spectroscopy (APPES). A wealth of information about the surface changes of materials is available around NAP conditions at different temperatures with soft and medium x-ray energy ranges (hv = 100-2000 eV). However, this is at the cost of loss of significant electron counts due to inelastic scattering with gas molecules present at high pressures. Higher the kinetic energy (KE) of the electron, better the chances of its survival at high pressures. In view of this fact, valence band (VB) photoemission was not explored with low photon energy, such as He I (hv = 21.2 eV), due to expected high inelastic scattering expected with low KE electrons.

In spite of the above listed problems, with a laboratory APPES (lab-APPES) fabricated by Prevac, Poland and installed at NCL, Pune, India, we are able to observe electrons with low KE (5-16 eV) at NAP condition of 0.3 mbar oxygen pressure and at different temperatures. High quality VB photoemission results were obtained for oxidation of metallic copper surfaces to cupric oxide (CuO) via cuprous oxide (Cu2O) (see Fig. 1). Importantly, we are able to map out the changes happening under reaction conditions at high pressures, but with very low KE electrons. A cartoon is shown in Figure 2 for the changes in colour of Cu surface, experimental setup etc. There are many advantages with the above innovation and they are listed below: (1) Low energy photons are associated with low line width and hence high resolution is achieved at NAP conditions. (2) Low energy photons have complementary photoionization cross sections compared to high energy photons, which allows us to determine the energy levels of various orbitals/bands that originate from different elements. (3) A combination of points 1 and 2, allows the researchers to map out the total VB electronic structure; hence the scope of lab-APPES is broadened to a significant extent. (4) A design employed in UV lamp (UVS40A2, Prevac) disables the high pressure entering into the He-lamp, and hence UV generation was possible at high pressures. High photon flux density (>1016 photons/s sr) also helps to increase the electron counts. (5) Double front cone pumping arrangement employed in R3000HP (VG Scienta, Sweden) analyzer improves the vacuum to 10-4 mbar in a very short distance from the sample surface at 0.3 mbar. This design helps to retain large number of low KE electrons at high pressures. To the best of our knowledge, both the last points are not available with many of the existing APPES systems. A communication article based on the above result is accepted in Analytical Chemistry and the full article is available online at http://pubs.acs.org/doi/full/10.1021/ac4041026.

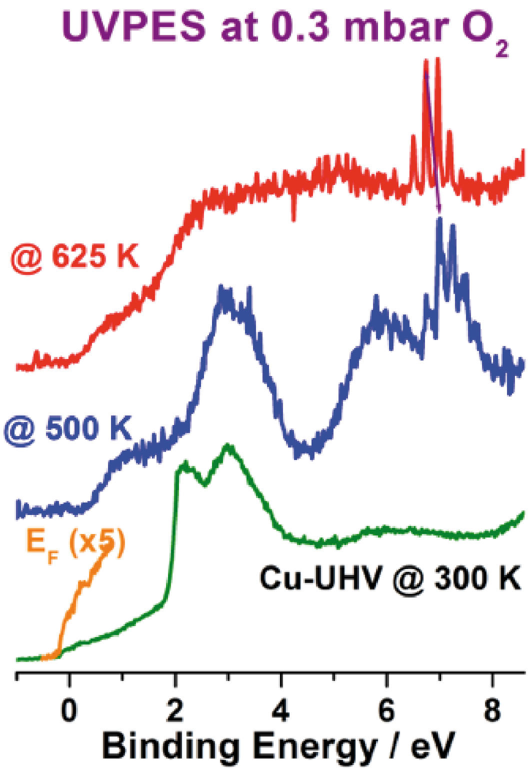

Figure 1. Valence band photoelectron spectra recorded with He I photons on Cu surface at different temperatures and 0.3 mbar O2 pressure. All the spectra were normalized at BE = 3 eV. Note the energy position of vibration features of molecular oxygen changes, as the surface changes from Cu2O at 500 K (blue trace) to CuO at 625 K (red trace), indicating the changes in surface work function.

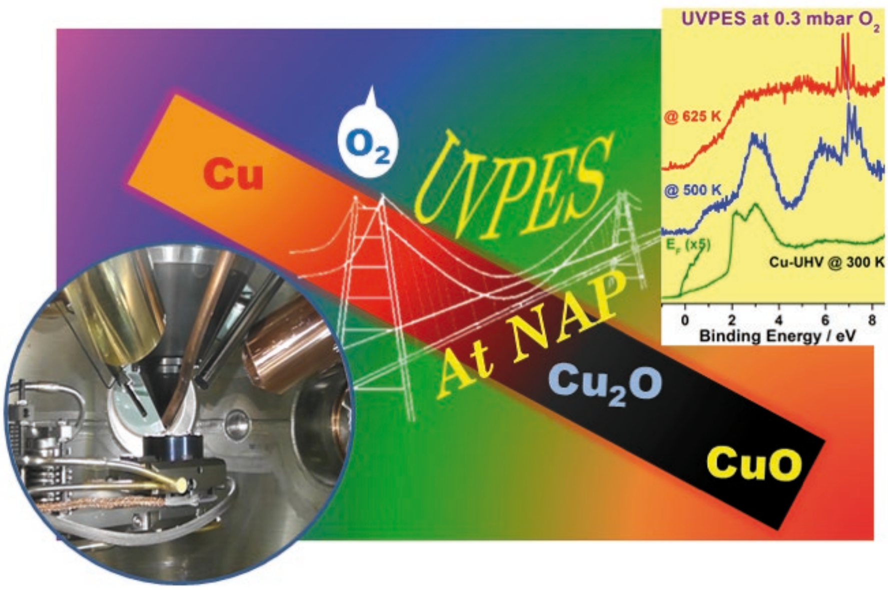

Figure 2. Changes in colour associated with copper surface from bright orange at ambient temperature to black as a function of temperature in 0.3 mbar O2 pressure. Inset shows the experimental setup and the spectra obtained