UV photoelectron spectroscopy at near ambient pressures: Mapping valence band electronic structure changes from Cu to CuO

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Abstract: Valence band (VB) changes, and hence electronic structure evolution was directly observed with low kinetic energy (KE) electrons at near ambient pressure (NAP) conditions with He I photon source in a custom built laboratory ambient pressure photoelectron spectrometer (Lab-APPES). Polycrystalline Cu-surfaces was gradually oxidized in O₂ to Cu₂O, mixture of Cu₂O + CuO and finally to CuO between 300 and 625 K and at NAP. Typical VB features for Cu, Cu₂O and CuO was observed and the results corroborate well with core level and Auger spectral changes. High mean free path associated with low KE electrons, very less or no inelastic scattering, and effective pumping and the design of electrostatic lens regime help to minimize the electron attenuation at NAP conditions. Present results extend the capabilities of APPES tool to explore the in-situ evolution of electronic structure of materials at NAP and high temperatures.

Keywords: Surface science, Photoelectron spectroscopy, Heterogeneous Catalysis, Electronic structure, APPES, Copper.
**Introduction**

Photoelectron spectroscopy (PES) is the direct experimental technique available to explore the valence band (VB) electronic structure (VBES) of solids and molecules directly and without any assumptions. VBES analysis provides wealth of information about the chemical bonding, hybridization and energy of different orbitals/bands, Fermi level ($E_F$) information etc. However, conventional PES works under ultra high vacuum ($\sim 10^{-10}$ mbar), and hence the changes that occur under working condition of materials (or closer to that), such as in catalysis, electrochemistry, cannot be explored by PES. Recent advances in the ambient pressure photoelectron spectroscopy (APPES) are of immense help to remove the above obstacle, and PES under near ambient pressures became possible. In fact, there is a sudden surge in reports in this area, especially in the area of heterogeneous catalysis since it is fully relevant. Nonetheless, extent of inelastic scattering of photoelectrons increases at near ambient pressure (NAP). Inelastic scattering depends on the inelastic mean free path ($\lambda$) and the kinetic energy (KE) of the electrons before it reaches a significant vacuum of $\leq 10^{-2}$ mbar in the electrostatic lens column. Under the above conditions, high KE electrons ($>100$ eV) can survive the near ambient pressures (0.1 - 10 mbar) due to $\lambda \approx$ few mm, and hence PES is possible with $h\nu \geq 100$ eV. Low KE electrons ($<100$ eV) were expected to attenuate even severely, and, in fact, there are no reports on the VBES analysis of solid surfaces with low energy photons at NAP conditions.

In contrast to the above facts and expectations, we demonstrate here the VBES mapping with low photon energy, He I ($h\nu = 21.2$ eV), and hence low KE electrons (5-16 eV) at NAP, up to 0.3 mbar. To the best of our knowledge, there are no such reports available in the literature to demonstrate the VB analysis of solid surfaces at NAP ($\geq 0.01$ mbar) conditions. All the experiments were carried out in a custom built Lab-APPES unit installed recently in our laboratory at CSIR-NCL, Pune. Design and performance aspects of above Lab-APPES unit was published recently, and oxidation of Cu, Ag and Au surfaces with $O_2$ under 1 mbar and temperatures up to 800 K was demonstrated through Lab-
In the following, we describe the VBES changes observed with polycrystalline Cu foil up to 0.3 mbar O$_2$ pressure and 625 K. VB spectra were recorded with conventional He I and AlK$_\alpha$ x-ray photon sources. VB changes observed due to oxidation are corroborated with core level changes in the oxidation state of Cu. It is to be noted that low energy photons offer the best possible resolution. Photoionization cross section ($\sigma$) of VB and core levels depends on the incident $h\nu$ and this is an extra handle to confirm the origin of different VB features.

**Experimental Methods**

Lab-APPES unit is a custom-built machine from Prevac, Poland to perform PES up to 1 mbar pressure in an open reactor design and equipped with VG Scienta’s R3000HP analyser, Al K$\alpha$ monochromator MX 650, and it has several other advantages. Above analyser is equipped with three differential pumping stages to maintain high vacuum during NAP experiments. Two sets of differential pumping are available in the electrostatic lens regime (ELR) and the third one is available in the electron energy analyzer (EEA). Distance between sample surface and aperture (of the cone, R = 0.4 mm) attached to ELR was maintained at 1.2 mm for all of the experiments reported. Further, a special design of double front cone pumping arrangement is available in the ELR (see Fig. S2 in Supporting Information). The main advantage with this design is a fast decrease in pressure with a steep pressure gradient from the aperture to the EEA. It is to be underscored that the first differential pumping records 2 x 10$^{-4}$ mbar when the analysis chamber is at 1 mbar. This helps to minimize the inelastic scattering of low KE electrons. Further, R3000HP employs the advanced concept of electron converging with an aperture free ELR. In contrast to the conventional ELR, electrostatic voltages in the R3000HP model analyzer is applied in such a way that they converge all the electrons. UV discharge lamp source (UVS40A2, Prevac) with photon flux of 10$^{16}$ photons/s sr was employed for measuring VB. XPS was measured using monochromatic Al K$_\alpha$ (1486.6 eV) source, unless otherwise stated.
Results and Discussion

VB spectra of Cu surfaces were recorded as a function of O$_2$ partial pressure and temperature and the critical results are shown in Fig. 1. Clean Cu-surface shows the typical 3d VB features between binding energy (BE) = 1.8 and 4.2 eV with distinct E$_F$. An increase in O$_2$ pressure up to 0.01 mbar at 300 K did not show significant changes. E$_F$ feature with comparable intensity as that of Cu-UHV-300 K was observed. Further increase in O$_2$ pressure begins to broaden the VB features. O$_2$ vibrational features begin to be observed ≥0.1 mbar O$_2$ pressure, and it was confirmed by control experiments with gas phase O$_2$ PES. At 0.3 mbar, a broad Cu 3d feature between 2 and 4 eV was observed with a low intensity, broad and featureless peak between 4 and 7 eV, due to chemisorbed oxygen. Secondary electrons increases at BE ≥ 10 eV and hence background intensity also increases.

On increasing the temperature gradually to 725 K at 0.3 mbar O$_2$ pressure (see wine red trace in Fig. 1 and Fig. S1 in SI), a complete oxidation of Cu$_2$O was observed; indeed, Cu to Cu$_2$O oxidation is complete at 500 K (Fig. S1 in SI). E$_F$ features disappear completely, and a characteristic narrowing of Cu 3d band was observed at 600 K (Fig. 1). A new feature at 1.3 eV develops, which is also very characteristic of Cu$_2$O. O 2p features between 4 and 7 eV at 300 K changes into a fully developed feature at 6 eV at ≥373 K. Above observations were corroborated with changes in Cu 2p core level, x-ray excited Auger electron spectra (XAES) and VB spectra recorded with AlKα (vide infra, Fig. 2). Due to hybridization of O 2p with Cu 4s and 4p orbitals in Cu$_2$O, there is a large energy gap between the fully filled Cu 3d$^{10}$ (3 eV) and O 2p (6 eV) was observed as a valley. Vibrational features of molecular O$_2$ overlap with the O 2p features at 6.7-8 eV. Further, BE of vibrational features of molecular O$_2$ shifts by 0.6 eV on Cu$_2$O compared to metallic Cu and the shift is indicated by a dotted arrow; this shift is attributed to the change in work function of metallic Cu to Cu$_2$O semiconductor. This also underscores that gas phase O$_2$ signatures are strongly influenced by the surface work function, and hence it should be very close to the surface. This critical observation fully confirms the presence of O$_2$ at indicated pressures and the in-situ nature of the experiments.
Valence band photoelectron spectra recorded with He I photons on Cu surface at different temperatures and up to 0.3 mbar O₂ pressure. All the spectra were normalized at BE = 3 eV (dashed line). Top two VB spectra, given in grey and black colour, were recorded at 625 K and 0.3 mbar O₂ pressure, but oxidized at 0.8 and 1 mbar O₂, respectively, prior to VB measurements.

Temperature dependent VB spectra recorded at 0.3 mbar O₂ demonstrates a gradual change in Cu-metal to Cu₂O (Fig. S1 in SI). However, an increase in temperature up to 800 K at 0.3 mbar O₂ partial pressure does not oxidize Cu₂O further (see Fig. S1 in SI). Even when 800 K at 0.3 mbar O₂ pressure was maintained for about 1 h, no further oxidation of Cu₂O to CuO was observed. In fact, from our earlier report it is clear that Cu oxidation is possible at higher pressures. Hence oxidation was carried out at 0.8 and 1 mbar O₂ pressure at 625 K, but the UVPES were recorded at 0.3 mbar pressure and at 625 K. Due to severe attenuation in photoelectron intensity ≥0.4 mbar, the above procedure was followed.

Figure 1. Valence band photoelectron spectra recorded with He I photons on Cu surface at different temperatures and up to 0.3 mbar O₂ pressure. All the spectra were normalized at BE = 3 eV (dashed line). Top two VB spectra, given in grey and black colour, were recorded at 625 K and 0.3 mbar O₂ pressure, but oxidized at 0.8 and 1 mbar O₂, respectively, prior to VB measurements.
First, high pressure dosing of O$_2$ at 0.8 and 1 mbar at 625 K was carried out, followed by VB spectra recording at 0.3 mbar O$_2$ pressure and 625 K demonstrate further oxidation of Cu$_2$O to CuO. A broadening of Cu 3d along with a shift in O 2p to lower BE eliminates the valley between the above features, observed for Cu$_2$O. Strong hybridization between Cu 3d and O 2p bands leads to the above energy changes and this is confirmed by changes in Cu 2p core level and x-ray excited Auger electron spectral (XAES) LMM KE. Fully resolved vibrational features of molecular O$_2$ were observed after complete oxidation to CuO. Vibrational features of O$_2$ shift by 0.15 and 0.1 eV with further oxidation due to 0.8 and 1 mbar treatment, respectively, underscoring the change in work function from Cu$_2$O to CuO. A simple comparison of present result with that of pure Cu$_2$O and CuO at UHV by Ghijsen et al$^7$ matches very well. It is also to be noted that earlier we reported on Cu oxidation to Cu$_2$O and CuO by APPES at 1 mbar O$_2$ pressure between 300 and 675 K; however, core level and VB changes were followed exclusively with XPS. It is evident from Fig. 1 that Cu to Cu$_2$O occurs at 0.3 mbar O$_2$ pressure. Further oxidation of Cu$_2$O to CuO requires higher pressures up to 1 mbar. Hence the high pressure (0.8 and 1 mbar) treatment was carried out, but the UVPES spectra were recorded at 0.3 mbar (Fig. 1), due to signal attenuation, as noted above. Present communication’s relevance stem from the fact that the evolution of direct electronic structure was addressed, such as, (a) overlap in energy levels of Cu 3d and O 2p bands in CuO which also underscores the strong hybridization between the two orbitals, however, no energy overlap between Cu 3d and O 2p for Cu$_2$O, (b) changes in surface work function from metallic Cu to CuO through shift in vibrational features of molecular oxygen, (c) changes in Fermi level features. All the above information was possible due to the high resolution with UVPES (26 meV) than XPS (420 meV). It is also to be noted that we could observe UVPES results with a conventional UV discharge lamp in a laboratory APPES system and without any shielding.

VB spectra shown in Fig. 1 is fully corroborated with the measurements made with Cu 2p core level, XAES of Cu-LMM level, and VB spectra recorded with Al Kα and the results are shown in
Fig. 2. Our earlier report on Cu oxidation at 1 mbar and different temperatures\(^4\) also gives similar results, but the results presented here are collected independently while collecting the data presented in Fig. 1. It is to be noted that top two set of spectra (Fig. 2a, b and c) was recorded first at 1 mbar (black traces) or 0.8 mbar (grey traces) and subsequently at 0.3 mbar O\(_2\) pressure, while maintaining the temperature at 625 K; however, no significant difference was observed within a set of results. This set of experiments was carried out exclusively to simulate the conditions employed in UVPES (black and grey traces in Fig. 1). BE and full width at half-maximum (FWHM) for Cu 2p\(_{3/2}\) core level from Cu (932.8 and 0.76 eV) and Cu\(_2\)O (932.4 and 0.95 eV) are not too different, but can be differentiated with different XAES LMM KE values as they appear at 918.8 and 916.8 eV, respectively.\(^4,8,9\) Cu\(_2\)O was partially oxidized to CuO at 0.8 mbar at 625 K (observed as shoulder at 933.8 eV) and a typical Cu 2p satellite features (940-945 eV) were observed along with a broad shoulder at 934 eV. Above broad shoulder develops into a complete feature at the cost of Cu\(_2\)O while O\(_2\) dosing at 1 mbar. Satellite features too grow strongly and demonstrates the oxidation of Cu\(_2\)O to CuO and it requires both high pressure (1 mbar) and temperature (625 K). Cu LMM also shows corresponding changes and it shifts to 918.2 eV on CuO formation.

VB spectra recorded with AlK\(\alpha\) are shown in Fig. 2c corresponds and complements well with the changes observed with UVPES results given in Fig. 1. Broad Cu 3d feature of metallic Cu gradually narrows down with a distinct feature at 1.2 eV on Cu\(_2\)O formation at 0.3 mbar O\(_2\) pressure between 500 and 800 K (wine red trace in Fig. 2c). A major change occurs in the VB spectrum on increasing the temperature to 625 K and pressure up to 1 mbar. VB broadens between 1 and 13.5 eV, and the typical Cu\(_2\)O feature at 1.2 eV decreases in intensity. Further, a broad feature is observed between 9 and 12.5 eV. Indeed, this feature is very characteristic for CuO and attributed to a satellite due to 3d\(^8\) final state configuration.\(^7,9\) Photoionization of 3d\(^9\) ground state configuration leads to the above satellite. Main VB feature observed at 3.5 eV, due to Cu 3d bands, overlap with O 2p feature
between 3.5 and 7.5 eV. Above energy overlap is attributed to the strong hybridization of Cu 3d and O 2p orbitals in CuO, which is typical for cuprates.\textsuperscript{7,9}

**Figure 2.** (a) Cu 2p\textsubscript{3/2} core level, (b) Cu LMM, and (c) VB spectra measured while Cu surface exposed to O\textsubscript{2} at NAP and at various temperatures. Dotted, dash-dot and solid lines indicate the position of Cu\textsuperscript{0}, Cu\textsubscript{2}O and CuO, respectively. Top two set of spectra in all panels was recorded first at 1 mbar (black traces) or 0.8 mbar (grey traces) and subsequently at 0.3 mbar O\textsubscript{2} pressure, while maintaining the temperature at 625 K. Spectra recorded at 1 and 0.8 mbar pressures are similar to that of the results recorded later at 0.3 mbar. Characteristic narrowing of 3d bands for Cu\textsubscript{2}O, and 3d\textsuperscript{8} satellite for CuO was observed in the VB spectrum highlights the changes in electronic structure can be mapped as a function of measurement conditions. Results presented here is similar to our earlier work (ref. 4) on Cu oxidation at 1 mbar O\textsubscript{2} and different temperatures.

Very different \(\sigma\) values for O 2p (0.00024 Mb) and Cu 3d (0.012 Mb) at \(h\nu = 1486.6\) eV helps to confirm the origin of VB features.\textsuperscript{5} Indeed, Cu 3d spectral weight is primarily observed in the VB at 2-4 eV for Cu, Cu\textsubscript{2}O and CuO and it is fully supported by the larger \(\sigma\) of Cu 3d, by about two orders of magnitude than that of O 2p. In contrast, O 2p (0.16 Mb) exhibits significantly higher \(\sigma\) than that of Cu 3d (0.10 Mb) at \(h\nu = 21.2\) eV. On Cu\textsubscript{2}O and CuO formation, an almost equal intensity of Cu 3d and O 2p features were observed in Fig. 1.
Results reported in Figs. 1 and 2 are as expected, and in agreement with literature results reported for Cu, Cu$_2$O and CuO;\textsuperscript{7,9} it suggests that there are no artefacts in the reported experiments and results. 1.2 mm distance was maintained between the sample and aperture makes it 1.5 D (D = aperture diameter = 0.8 mm), constant O$_2$ pressure, as well as in-situ heating of O$_2$ to the measurement temperatures avoids any artefacts. Shift in vibrational features of molecular O$_2$ due to changes in work function of Cu, Cu$_2$O and CuO fully support the reliability of measurements at NAP. Possible reasons for the observation of low KE electrons are given below.

Calculation of inelastic mean free path, $\lambda_m$ (m = monolayers, ML), within solids by Seah and Dench\textsuperscript{10} method were made (see SI). It shows $\lambda_m = 3.9$ ML (4.6 ML) with a KE of 13 eV (550 eV) for metallic Cu at BE = 3 eV in Fig. 1 (BE = 933 eV in Fig. 2a). Up on Cu$_x$O formation, $\lambda_m$ increases to 14 ML (8.1 ML) for KE = 13 (550) eV. $\lambda_m$ calculated for low KE electrons is comparable for metal and higher for oxides than that of 550 eV electrons; this indicates the possibility of survival of low KE electrons at high pressures better than its high KE counterparts. This is further testified by comparable S/N ratio observed in Figures 1 and 2. Due to low penetration depth of He I than AlK$\alpha$ photons, the present VB analysis is exclusively limited to top 1-2 surface atomic layers, and hence above $\lambda_m$ values are sufficient to survive the NAP conditions for about 2 mm. It is to be noted that the density of a gas at 0.1-1 mbar and 298 K is six-seven orders of magnitude smaller than for a condensed solid. This translates into $\lambda \approx$ mm for low KE electrons in gas pressures of 0.1-1 mbar.\textsuperscript{1b} However, when the distance increases >1.2 mm between aperture and sample surface, electron counts decreases drastically and >1.5 mm no electron counts was observed, except for vibrational features of O$_2$.

No significant inelastic scattering occurs in the region of interest with KE = 7-16 eV (BE = 9-0 eV), which would otherwise attenuate the electrons severely. However, elastic scattering and rotational and vibrational cross section are expected to contribute significantly with low KE electrons. Elastic scattering would drift some electrons and hence they cannot be transmitted, and
Figure 3. Photograph of the open-reactor design employed in Lap-APPES unit. Sample holder can be moved up to the aperture of the front cone attached to ELR. Gas doser can be heated to heat the input gas to minimize the temperature difference between spectral measurement and gas temperatures.

hence a decrease in some electron counts is expected. Rotational and vibrational cross section, at the best, could broaden peaks in VB spectrum due to energy loss of few meV. Our observations and conclusions are in very good agreement with the theoretical calculations of predominant elastic and rotational cross sections for low energy electrons, with no significant contribution from inelastic scattering. In spite of the large difference in KE of photoemitted electrons that originate due to UV or X-ray source, very low or no inelastic scattering characterises the low KE electrons. It is also to be noted that the photon flux of He I is $10^{16}$ photons/s.sr and about three to four orders of magnitude higher than AlKα and helps towards higher counts under comparable conditions (see Figs. 1 and 2). Under present NAP conditions, S/N ratio is decided by large electron attenuation with high KE electrons; however, in spite of low KE electrons, better S/N was managed due to high photon flux of He I with some elastic scattering and rotational cross section.

Double front cone design employed in ELR improves the vacuum from aperture, as it is pumped by both first and second differential pumps in the lens column (see Fig. S2 in SI). Further, electron
energy analyser (R3000HP) is an aperture free lens column, which effectively increases the transmission and contributes for better quality results.\textsuperscript{4,12} It is also to be noted that the open reactor design was employed in the present Lab-APPES unit and sample surface can be practically moved up to the aperture, as shown in the photograph (Fig. 3). Capillary gas doser also can be moved up to the sample surface and the pressure near the sample surface is measured through a CTR gauge (not shown in Fig. 3). Pressure measured with the CTR gauge corresponds well with the pressure measured in other gauges, kept far away from sample surface. This arrangement fully ensures the reliability of NAP values reported in this communication.

Through observation of low KE electrons at NAP and at high temperatures, possibility of following valence band electronic structure under near working conditions of catalysts and materials is established. Cu surface was systematically oxidized to Cu$_2$O, mixture of Cu$_x$O, and finally to CuO. Results observed in VB with low KE electrons are corroborated with that of results observed from high KE electrons, such Cu 2p core level. Insignificant inelastic scattering and high photon flux helps to observe low KE electrons and hence VBES. We believe similar observation is possible with other Lab-APPES and APPES systems. Better quality results, than the present set of results, are possible with high brilliance photon sources and it is worth exploring.

ASSOCIATED CONTENT
Supporting Information
Description about Lab-APPES unit, IMFP calculation equations, temperature dependent UVPES valence band spectra at 0.3 mbar (Fig. S1), and schematics of electron energy analyzer (Fig. S2). This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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