

Supplementary Information

The effect of covalently bonded aryl layers on the band bending and electron density of SnO₂ surfaces probed by synchrotron X-ray photoelectron spectroscopy

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XPS measurements and resolution

X-ray photoelectron spectroscopy (XPS) spectra was collected in the soft x-ray beamline of the Australian Synchrotron, at room temperature, and pressures better than 2×10^{-10} mbar. The purpose and strength of this work was to use the variable photon energy capabilities of the beamline to probe the same depth into the material for all core levels. This approach allows comparing the effect of the modifier films across different elements, since the measured signals result from sampling the same number of atomic layers below the surface regardless of the binding energy associated to each element. To this purpose, the scans were collected at a photon energy 150 eV higher than the corresponding core level, thus resulting in a sampling depth of ~ 6.2 Å for all elements.¹

Spectra were collected at normal incidence using a Specs Phoibos 150 hemispherical electron energy analyzer and slit size of $5.7 \times 20 \mu\text{m}^2$ or $5.7 \times 10 \mu\text{m}^2$. Under these conditions the measured resolution at a photon energy of 401 eV is better than 74 meV, in close agreement to that of theoretical calculations.²

The overall spectral resolution of the system is determined by the angular positioning of the monochromator mirrors and gratings at the in the soft X-ray beamline of the Australian Synchrotron and by beam fluctuations associated with the storage ring. As a consequence, the resolution is dependent on the photon energy, and increases with decreasing photon energy from 80 meV at 680 eV to 20 meV at 150 eV.

A conservative step size of 100 meV was thus adopted for all the core level scans in this work, while survey scans were collected at 500 meV step.

XPS discussion and analysis

The effect of the Sn-O-C contribution to the valence band (VB) edge was assessed similarly to previous works³ by multi-peak modelling the VB spectra, to rule out possible broadening of the VB tail that could affect the extracted values of band bending. For each modified sample, a modelled VB spectrum was obtained by combining the contributions from the multi-peak fit of the data and reconstructing the VB spectrum after reducing the weight of the Sn-O-C – related emission. The effect of this contribution on the band bending was then explored by fitting the edge of the modelled spectrum and extracting new values of ζ .

Figure S1 shows that decreasing the Sn-O-C contribution has no effect on the overall VB edge, resulting in changes of ζ smaller than the spectral resolution, and comparable with the error associated with the fitting method. The possibility of broadening the tail of the valence band (VB) spectra due to contributions associated to the surface modification process is therefore ruled out.

Finally, it is worth noting that while the band bending manifests in spectral shifts of both core levels and valence band edge, the significantly higher spectral resolution obtained at lower energies makes it more reliable to determine band bending shifts at low photon energies using the VB edge, than relying on core level spectra such as Sn3d.

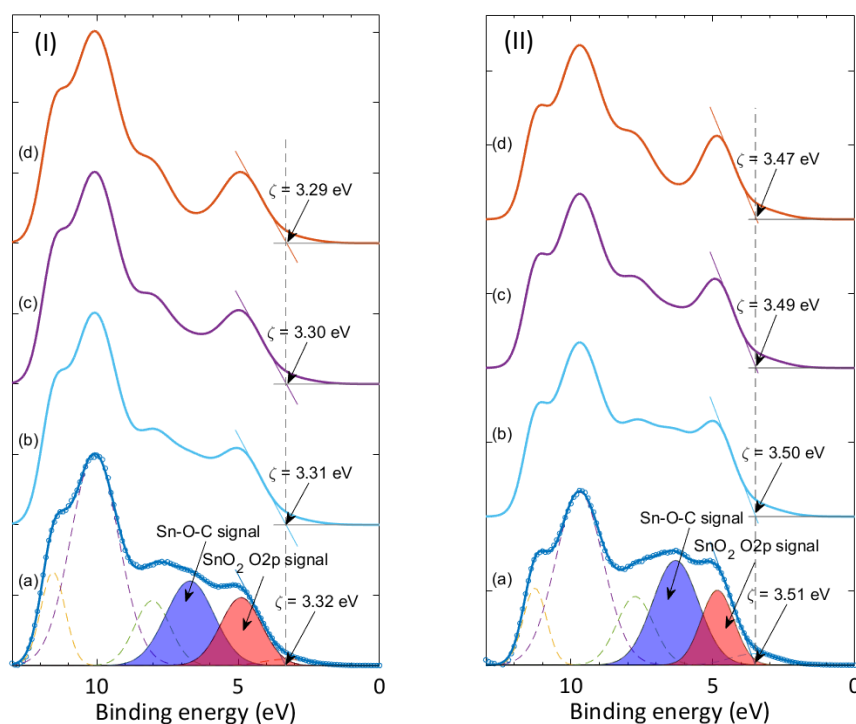


Figure S1. Measured and modelled VB spectra of electrochemically modified (I) and spontaneously modified (II) SnO₂ (101) surfaces showing the effect of the Sn-O-C signal on the valence band edge. (a) Measured VB spectra at $h\nu = 150$ eV and corresponding multi-peak fit, showing the Sn-O-C signal does not overlap the VB edge, thus being unlikely to have a significant effect on the extracted value of ζ . (b), (c), (d) Multi-peak modelling of the VB spectra based on the multi-peak fit shown in (a), after reducing the Sn-O-C signal by 25%, 50% and 75%, respectively. Linear fits of the corresponding VB edge and extracted values of ζ are included, showing that the variations in the extracted value of ζ are smaller than the spectral resolution, and commensurable with the error associated with the fitting method.

References

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