

Electronic supplementary information (ESI) for

Formation of an Extended Interphase Layer During Deposition of Cobalt onto Tetraphenylporphyrin: A Hard X-Ray Photoelectron Spectroscopy (HAXPES) Study

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1. C 1s X-ray photoelectron spectra

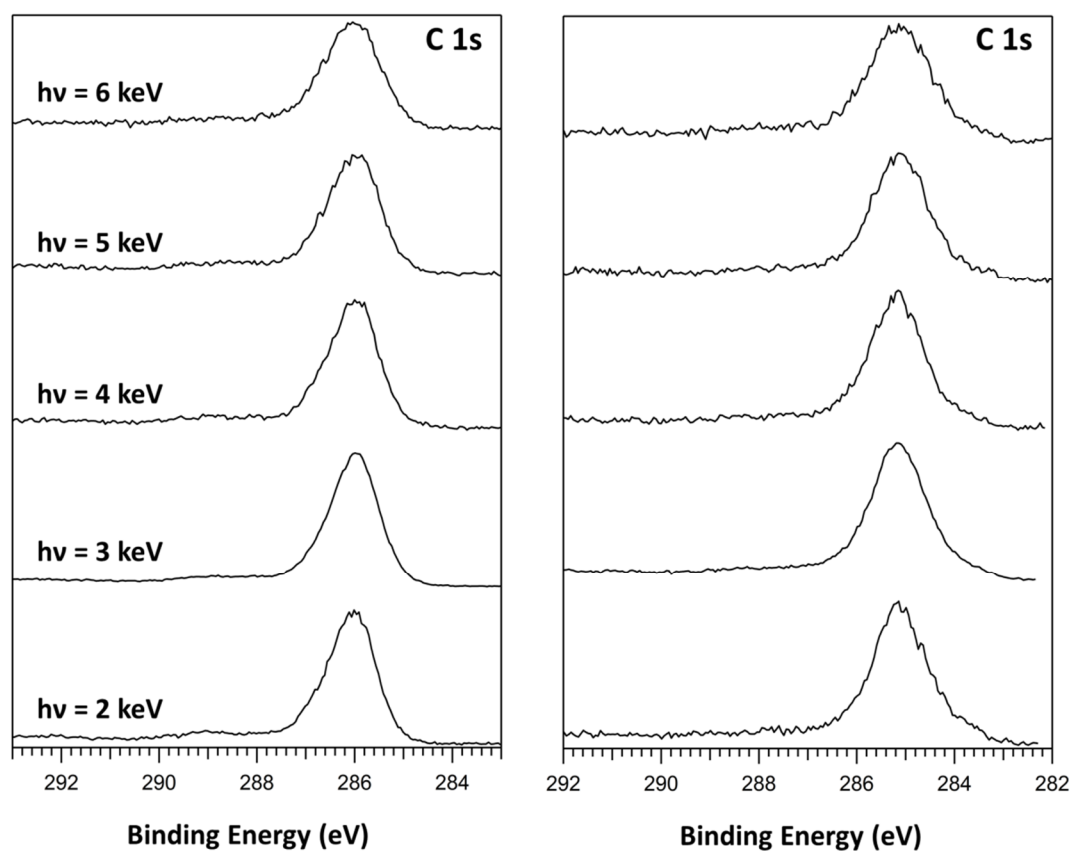


Figure S1. C 1s XP spectra of a pristine 18 nm 2HTPP layer, taken before (left panel) and after (right panel) vapor deposition of 1.8 nm Co. From bottom to up, spectra were taken with different photon energies as indicated. Electrons were collected at 0° relative to the surface normal.

2. Interface roughness

Derivation of the depth distribution of the reacted interphase layer (here CoTPP) is straightforward only for a flat interface (Figure S2a). In this case, the concentration vs. depth profile $c_r(z)$ derived from HAXPES (red line) correctly shows the abrupt interface between the interphase layer (CoTPP) and the underlying pristine 2HTPP.

For a rough, buckled interface, the situation is more complicated. In the simple model shown in Figure S2b, a HAXPES experiment in normal emission geometry would detect two different thicknesses, as visualized by the black arrows representing the electron trajectories. As a result, the concentration vs. depth profile $c_r(z)$ would show two steps (red line). In the case of a real rough interface with a distribution of different angles between the emission direction (black arrows) and the orientation of the reacted layer, a gradual decrease of $c_r(z)$ would result (green dotted line). Therefore, even if the CoTPP/2HTPP interface is locally abrupt (as in Figure S2b), the experiment would yield a concentration profile that is identical to one of a diffuse interface (with partial intermixing of CoTPP and 2HTPP).

Conversely, if the HAXPES analysis shows an abrupt interface, then the interface is not only abrupt, it is also laterally sufficiently uniform for the application of a spatially integrating spectroscopic technique.

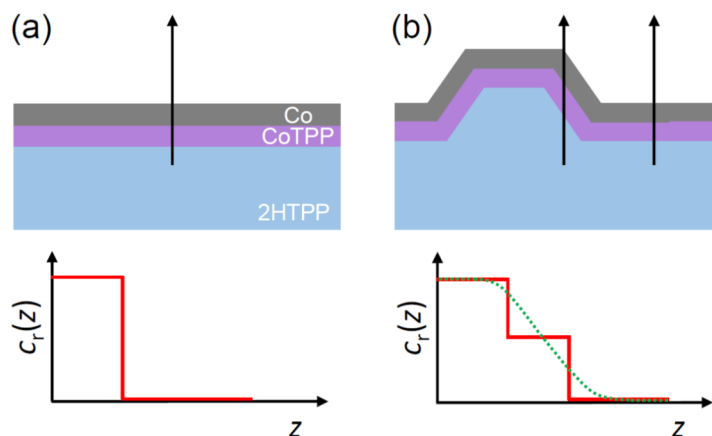


Figure S2. (a) HAXPES on a flat layer-by-layer interface in normal emission geometry (as indicated by the black arrow). The concentration vs. depth profile, $c_r(z)$, of the reacted component, CoTPP, is shown below (red line). (b) Corresponding model for a buckled layer-by-layer interface. The concentration vs. depth profile (red line) now has two steps because there are two apparent thicknesses of the reacted layer (CoTPP). For a real buckled interface with a distribution of different angles between the emission direction and orientation of the reacted layer, a gradual decrease of the apparent concentration would result (green dotted line).

However, it should be noted that the sensitivity of the normal-emission HAXPES experiment to surface roughness is rather moderate. The reason for this is that any inclination of the actual surface (due to roughness) by an angle $\Delta\theta$ relative to the normal emission direction will increase the path length of the photoelectrons by the factor of $1/(\cos\Delta\theta)$. Outside normal emission geometry, this effect is larger due to the shape of the cos function. This has also been experimentally verified in previous work.¹ Calculations for the roughness induced increase of the photoelectron path lengths are given in Section 2.1 of the paper.

References

1. S. V. Merzlikin, N. N. Tolkachev, T. Strunskus, G. Witte, T. Glogowski, C. Wöll and W. Grünert, *Surf. Sci.*, 2008, **602**, 755-767.