

Metal—Organic Coordination Interactions in Fe—Terephthalic Acid Networks on Cu(100)

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Supporting Information

Here we provide further information regarding the peak fitting for the Fe 3p data presented in Figure 3.

We find that the Fe 3p spectra for the Fe multilayer film in Fig. 3a(vi) can be properly fitted by using only two components at 52.8 and 52.0 eV, as revealed by the low fitting residual. The two components have a relative area ratio of 0.70. The shape and position of this peak and the two peak fit are consistent with previous XPS studies on metallic Fe⁰ thin films.²⁵ This relatively simple two peak fit neglects the underlying complexity of the Fe 3p peak structure due to electron exchange interaction and electron correlation effects which have been explored in detail previously.^{17, 26, 27}

The coordination of the Fe atoms to the TPA molecules leads to a different Fe 3p photoemission feature which is shifted to higher binding energy with respect to the Fe metal peak. In order to fit this new feature, we assume that the Fe 3p photoelectron emission spectrum should have the same structure for coordinated Fe as for the metallic Fe. This is a reasonable choice, supported by the fact that the detailed photoemission structure has been shown to be unchanged for iron oxides and other iron compounds compared to metallic iron.^{13, 15, 27}

Based on this assumption, spectra (i-v) were each fit with two sets of the peak pair fitted to (vi). In the case of (v), the positions of the peak pairs as well as the relative area of the two peaks within

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each pair was free to vary for the fit optimization, but the peak shape parameters as well as the separation of the peak pairs were held constant at the values which fit spectrum (vi). Spectrum (v) is fitted very well by the two peak pairs and the resulting position of the peak pair for the metallic Fe agreed exactly with (vi), but the area ratio of the peaks within the pairs was somewhat different (0.96). In the subsequent fits of (i-iv), where the signal to noise ratio is smaller compared to (v, vi), the position of the metallic Fe peak pair, as well as the area ratio of the peaks within each pair were held constant, but the position of the second peak pair was free to move in the fits. Best fits were obtained with the latter pair of peaks at 54.1 and 54.9 eV (± 0.1 eV), respectively, for each of the spectra (i-v).

Alternatively, one can consider a more simplified approach to the peak fitting of Fig. 3a(i-v), which is to simply fit the coordinated Fe feature to a single peak. In doing so we find that we must use a very broad peak with Gaussian width of 2.9 eV (compared to < 1.2 eV for the Fe metallic features discussed above), indicating that this is most likely an oversimplification of a more detailed peak structure. The details of this structure certainly include the electron exchange and correlation features acknowledged above, but may also include multiple photoemission features due to slightly different Fe coordination geometries. Whether we choose to use this simplified fit approach or the more detailed peak pair discussed above, we find the same result for the position of the coordinated Fe photoemission and the same trends in peak size with increasing Fe coverage. Therefore, we have chosen the two peak fit because it has the stronger physical justification, especially since it is clear from the width of the coordination peak that it is not a single photoemission feature, and since there is to our knowledge no physical justification to neglect *a priori* the electron exchange and correlation effects for the coordinated Fe atoms.