surfaces

MDPI

Supplementary Material

4-Mercaptobenzoic Acid Adsorption on TiO_2 Anatase (101) and TiO_2 Rutile (110) Surfaces

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Calculation of depth of overlayer of mercaptobenzoic acid (MBA) on the titania surfaces.

Depth of the overlayer assumed a continuous film on the surface of the signal crystals. The inelastic mean free path of 100 eV photoelectrons passing through the MBA overlayer, λ_M was calculated using the NIST electron attenuation depth software to be 0.65 nm.

We then assumed a simple two-layer model, as shown in Figure S1, to calculate the depth of the film using the relative intensities of the O peaks from the molecule and the titanium dioxide surface. This means we do not have to consider factors such as photoionisation cross section, or sampling depth and transmission function of the analyser since the kinetic energies of the electrons from the two oxygen environments will be similar. Note for the atom number density for MBA we used crystallographic data for benzoic acid as no reliable data could be obtained for benzoic acid.

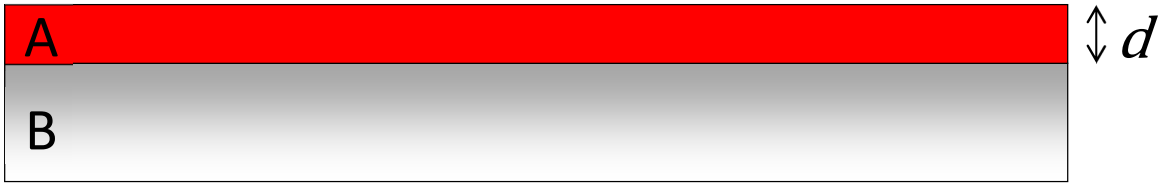

Figure S1. Diagram of the simple two-layer model used in the calculation of surface coverage of MBA on the two titania surfaces. d_A is the thickness of the MBA overlayer. A is MBA and B the titania crystal.

Equation S1 was used to determine the thickness of the overlayer.

$$\frac{I_A}{I_B} = \frac{X_A}{X_B} \frac{\left\{1 - \exp\left(-\frac{d_A}{\lambda_A(E_A)cos\theta}\right)\right\}}{\exp\left(-\frac{d_A}{\lambda_A(E_B)cos\theta}\right)} \quad \text{(S1)}$$

Where I_A = intensity of O 1s in MBA after dosing, I_B = intensity of the O 1s in TiO_2, θ = the emission angle relative to the surface normal = 0, so that the cos term = 1, λ_M = inelastic mean free path in overlayer, calculated using the TPP-2 formula [1,2] to be 0.65 nm, and d_A = the thickness of the overlayer in nm and X_A and X_B the number density of O atoms in MBA and TiO_2 respectively. X_A for MBA is 6.5 atoms/nm^3. X_B for rutile TiO_2 is 33 atoms/nm^3 and for anatase 42 atoms/nm^3. This gives an approximate thickness of 0.7 ± 0.1 nm on anatase and 0.6 ± 0.1 nm for rutile for both short (20 min) and long (≥2 h) deposition times.

A simple molecular picture of MBA gives a molecule size of ~0.8 nm thus the obtained thickness is consistent with the formation of a single layer of molecules at the surface. Even with the 70° tilt angle obtained in NEXAFS.

References

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2. Briggs, D.; Seah, M.P. Practical Surface Analysis (Second Edition), Volume 1- Auger and X-ray Photoelectron Spectroscopy, 2nd ed.; John Wiley and Sons Ltd.: Chichester, UK, 1990.