An Experimental Investigation of the Adsorption of a Phosphonic Acid on the Anatase TiO_2(101) Surface

Michael Wagstaffe,[†] Andrew G. Thomas,[*,‡] Mark. J. Jackman,[†] Maria Torres-Molina,[¶] Karen L. Syres,[§] and Karsten Handrup[‖]

[*]To whom correspondence should be addressed

[†]School of Physics and Astronomy, The University of Manchester, Oxford Road, M13 9PL, UK

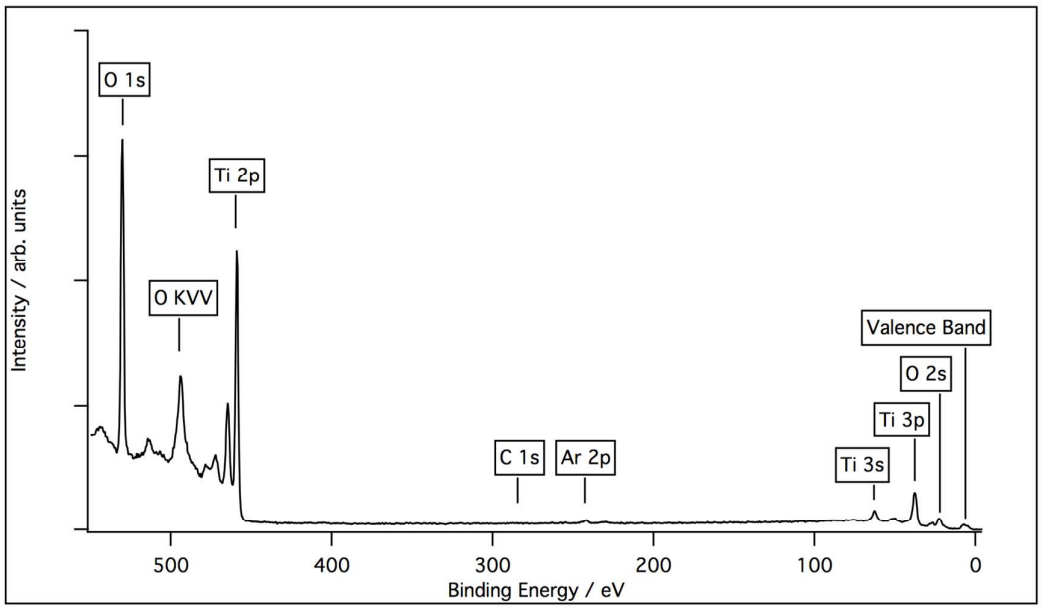
[‡]School of Materials and Photon Science Institute, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK

[¶]School of Chemistry, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK

[§]Jeremiah Horrocks Institute, The University of Central Lancashire, Fylde Road, Preston,PR1 2HE, UK

[‖]MaxLab, Ole Romers Vag, Lund, Sweden

S.1. Shows the survey scan recorded from the anatase TiO_2(101) surface, at 1000 eV photon energy, following cleaning by repeated sputter and anneal cycles. No surface contamination is observed other than a small amount of residual argon from the sputtering procedure.



S.2. Details of the calculation used to determine the surface coverage of PPA on anatase TiO_2(101) and the quantitative definition of a monolayer

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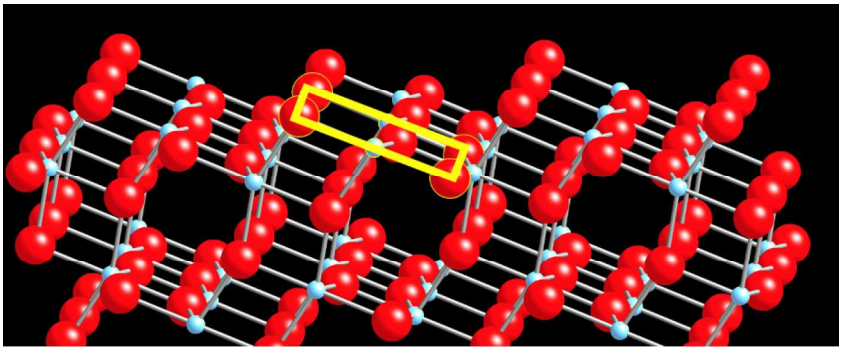
Catechol is known to saturate at monolayer coverage at room temperature, [1,2] therefore by comparing the C 1s:Ti 2p ratio in the catechol spectra to that of the PPA spectra, the coverage of PPA on anatase TiO_2(101) can be estimated. This method assumes that PPA adsorbs on to the anatase TiO_2(101) surface in a similar manner to catechol, i.e. through two oxygen atoms to neighboring Ti 5c atoms. The following equation has been used. [1]

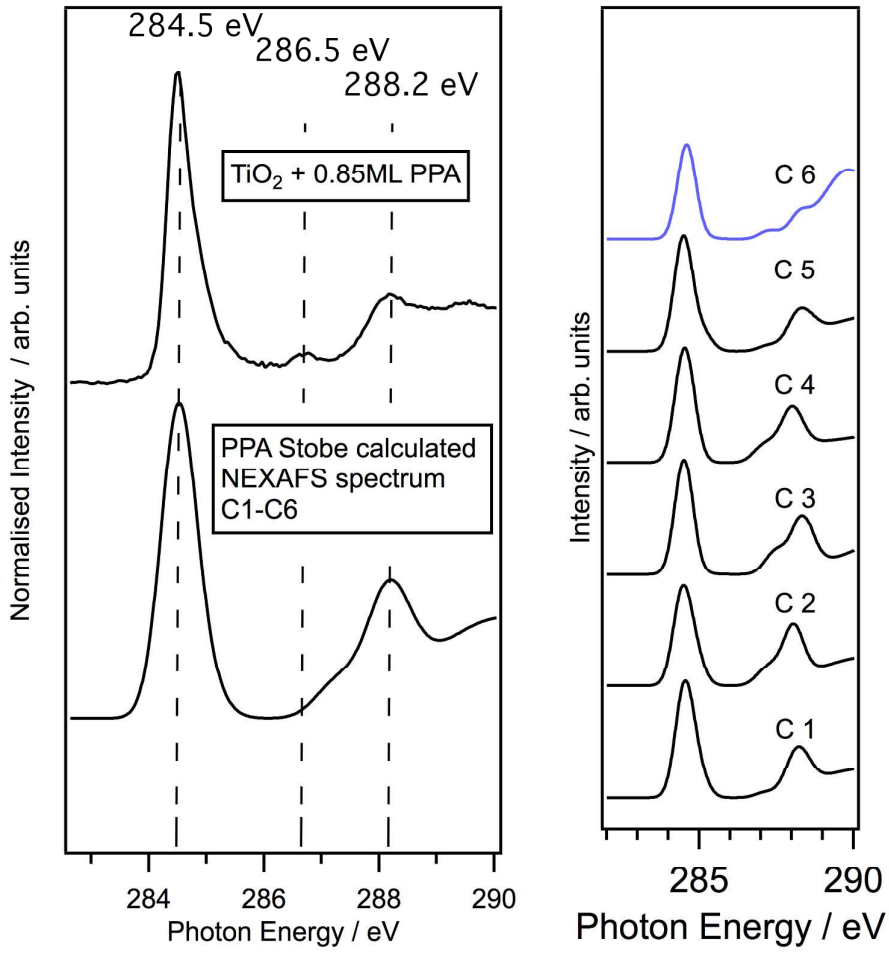
$$\%\ ML = \frac{I_{C\ 1s}/I_{Ti\ 2p}}{I_{C\ 1s\ (catechol)}/I_{Ti\ 2p\ (catechol)}} \times 100$$

	Ti 2p total peak area	**C1s total peak area**	**C 1s/Ti 2p**	**% ML**
Catechol ML coverage	4,744.95	3,836.10	0.81	100
PPA Dose 1	8,189.10	965.60	0.12	~15
PPA Dose 2	32,365.80	21,651.10	0.67	~85

Below is a picture of the anatase (101) surface. In order to gain a quantitative approximation for monolayer coverage we defined the surface unit cell as highlighted by a yellow rectangle below. This has an area of 14.9**Å^2** and contains a single Ti 5c atom. Since we are assuming that 1 molecule binds to two Ti 5c atoms, this means each "unit cell" contains 0.5 molecules at monolayer coverage. Therefore we can define 1 ML as 0.03 molecules/ **Å^2.**



S.3. A graph showing the expanded NEXAFS spectra, highlighting the asymmetry of the main π* peak



(1) Syres, K. L.; Thomas, A. G.; Flavell, W. R.; Spencer, B. F.; Bondino, F.; Malvestuto, M.; Preobrajenski, A.; Grätzel, M. Adsorbate-induced modification of surface electronic structure: pyrocatechol adsorption on the anatase TiO_2 (101) and rutile TiO_2 (110) surfaces. *J. Phys. Chem. C* **2012**, *116*, 23515–23525.

(2) Li, S.-C.; Wang, J.-g.; Jacobson, P.; Gong, X.-Q.; Selloni, A.; Diebold, U. Correlation between bonding geometry and band gap states at organic–inorganic interfaces: catechol on rutile TiO_2 (110). *J. Am. Chem. Soc.* **2009**, *131*, 980–984.