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Adsorption structure of glycine on TiO_2(1 1 0): A photoelectron diffraction determination

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ABSTRACT

High-resolution core-level photoemission and scanned-energy mode photoelectron diffraction (PhD) of the O 1s and N 1s states have been used to investigate the interaction of glycine with the rutile TiO_2(1 1 0) surface. Whilst there is clear evidence for the presence of the zwitterion $NH_3^+CH_2COO^-$ with multilayer deposition, at low coverage only the deprotonated glycinate species, NH_2CH_2COO is present. Multiple-scattering simulations of the O 1s PhD data show the glycinate is bonded to the surface through the two carboxylate O atoms which occupy near-atop sites above the five-fold-coordinated surface Ti atoms, with a Ti–O bondlength of 2.12 ± 0.06 Å. Atomic hydrogen arising from the deprotonation is coadsorbed to form hydroxyl species at the bridging oxygen sites with an associated Ti–O bondlength of 2.01 ± 0.03 Å. Absence of any significant PhD modulations of the N 1s emission is consistent with the amino N atom not being involved in the surface bonding, unlike the case of glycinate on Cu(1 1 0) and Cu(1 0 0).

1. Introduction

So far there have been very few structural studies of the adsorption of amino acids at well-characterised surfaces, with the only fully quantitative structure determinations being restricted to those of glycine, NH_2CH_2COOH on Cu(1 1 0) and Cu(1 0 0) [1–3], and of alanine, $NH_2CH_3CHCOOH$ on Cu(1 1 0) [4], achieved by scanned-energy mode photoelectron diffraction [5,6]. In all three of these cases, the acid is deprotonated by interaction with the Cu surface to form, respectively, glycinate (NH_2CH_2COO) and alaninate (NH_2CH_3CHCOO) species that bond to the surface through both of the carboxylate O atoms and the amino N atom, all three atoms occupying single-coordinated sites. This bonding configuration is consistent with a number of studies using electronic [7,8] and vibrational spectroscopy [9–11], and also scanning tunnelling microscopy [12–17] and density functional theory (DFT) calculations [18,19]. Some of these spectroscopic studies, however, do indicate that at different surface coverages, or in less well-ordered overlayers, other chemisorption bonding configurations probably occur involving only one or both of the carboxylate O atoms.

Insofar as one motivating factor for such studies is the issue of biocompatibility in medical implants, studies of TiO_2 surfaces are potentially more relevant, as many such implants are based on (surface-oxidised) titanium metal or composite ceramics including titania. Much the most studied surface of titania is that of rutile TiO_2(1 1 0), and there has been a small number of investigations of amino acids, and particularly glycine, on this surface. Important structural differences between the clean surfaces of Cu(1 0 0) and Cu(1 1 0) on the one hand, and of TiO_2(1 1 0) on the other hand, suggest that glycinate, if formed on TiO_2(1 1 0), is unlikely to bond in the same 'lying down' configuration through both the carboxylate O atoms and the amino N atom. The Cu–Cu nearest-neighbour distance on both Cu surfaces is 2.55 Å, quite similar to the O–O distance in carboxylates of ~2.27 Å; the spacing of the undercoordinated (five-fold-coordinated) Ti atoms on the TiO_2(1 1 0) (1 × 1) surface is somewhat larger (2.96 Å), but it is well-established that the simplest carboxylate species, formate (HCOO), does bond to adjacent pairs of these Ti atoms on this surface in a symmetric fashion (Fig. 1) with the O atoms some 0.3 Å off-atop and the O–O distance equal to 2.39 ± 0.08 Å [20]. Perpendicular to this carboxylate O–O alignment, however, the metal–metal atomic distances on the three surfaces are very different, namely, 2.55 Å (Cu(1 0 0)), 3.61 Å (Cu(1 1 0)) and 6.50 Å (TiO_2(1 1 0)). The match of this metal–metal distance to the separation of the amino N atoms from the O–O axis in the glycinate species is closest on the Cu(1 0 0) surface, such that all three bonding atoms lie quite close to atop sites [3]. On Cu(1 1 0) the larger Cu–Cu spacing leads to the carboxylate O atoms being significantly offset (by ~0.8–1.0 Å) from atop, but still in singly-coordinated sites [3]. On

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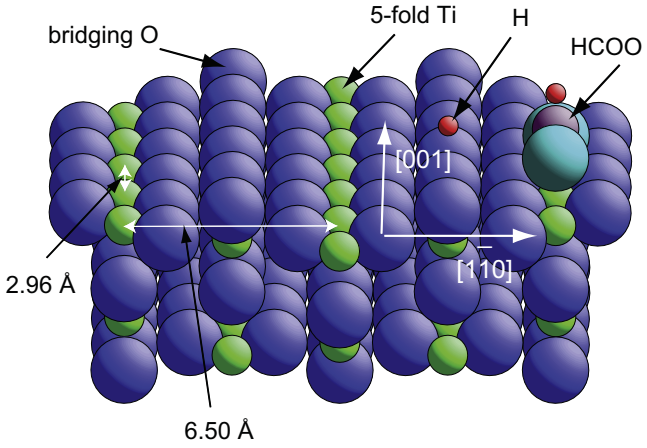

Fig. 1. Schematic diagram of the TiO_2(1 1 0) surface showing the dimensions of the unit mesh, the principle surface azimuthal directions, and the local adsorption geometry of the formate species (HCOO) and the coadsorbed H resulting from interaction with formic acid. O atoms are shown with larger atomic radii (blue) than the Ti atoms (green). (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

TiO_2(1 1 0)(1 × 1), however, the mismatch is very much larger, and the possibility of N bonding to an adjacent Ti atomic row is further hindered by the intervening row of bridging O atoms that lie higher above the surface (Fig. 1). It seems clear, therefore, on purely geometric grounds, that glycinate cannot bond to TiO_2(1 1 0) through all three molecular sites, and at most two of these sites, either the two carboxylate O atoms or one carboxylate O atom and the amino N atom, can be involved in the surface bonding.

The first surface science study of the TiO_2(1 1 0)/glycine system [21,22] was concerned mainly with photon-stimulated desorption and dissociation using photons in the energy range from 20 to 120 eV, but ultra-violet photoemission spectra were interpreted as indicating that in multilayer films the glycine is in the zwitterionic form ($NH_3^+CH_2COO^-$) that is also found in solid glycine. More recently, a STM investigation of this system [23] identified a local (2 × 1) ordering of molecular features on the surfaces; this is the same ordering seen for a number of simple carboxylate species including formate. This led the authors to propose that the local bonding configuration is similar to that of formate, with glycinate species bonded symmetrically to an adjacent pair of five-fold-coordinated surface Ti atoms through the two carboxylate O atoms with the molecule approximately perpendicular to the surface. This interpretation was reinforced by their observation that the STM images showed no evidence of any asymmetry in the molecular features. An experimental investigation of proline, C_4NH_8COOH, on the stoichiometric TiO_2(1 1 0) surface, using core-level photoemission [24,25], also indicates that both zwitterionic and dissociated (deprotonated) forms are present on the surface, but with the zwitterion desorbing at a lower temperature. Combined with the earlier results on glycine adsorption, the experiments therefore indicate that the preferred form of these adsorbed amino acids on TiO_2(1 1 0) is the deprotonated form, with zwitterionic material being present only at higher coverages, particularly in multilayer films. However, this conclusion is in conflict with that of a DFT investigation of the TiO_2(1 1 0)/glycine system. Specifically, Ojamäe et al. [26] identified the lowest energy structure as that of zwitterionic glycine, rather than glycinate (coadsorbed with atomic hydrogen), with the carboxylate O atoms bonded to five-fold-coordinated Ti atoms, but with the molecule tilted to form hydrogen bonds between the ammonia H atom(s) and the adjacent row of bridging O atoms. Other recent DFT and molecular dynamics calculations have been of larger amino acids in aqueous solution, thus modifying the relative stability of the zwitterion [27,28] and rendering the results less relevant to UHV experiments.

Here we show, using a combination of soft X-ray photoelectron spectroscopy (SXPS) and PhD, that at lower coverages (below those of multilayers), glycine reacts with the TiO_2(1 1 0) surface to form coadsorbed glycinate and atomic hydrogen, the glycinate bonding through the two carboxylate O atoms to a pair of five-fold-coordinated surface Ti atoms, while the atomic H bonds to bridging oxygen atoms to form a local hydroxyl species. Our results confirm the presence of the zwitterionic form of glycine at high (multilayer) coverages, but explicitly exclude the zwitterionic model of Ojamäe et al. at low coverage.

2. Experimental details

The experiments were conducted in an ultra-high vacuum surface science end-station equipped with typical facilities for sample cleaning, heating and cooling. This instrument was installed on the UE56/2-PGM-2 beamline of BESSY II which comprises a 56 mm period undulator followed by a plane grating monochromator [29]. Different electron emission directions can be detected by rotating the sample about its surface normal (to change the azimuthal angle) and about a vertical axis (to change the polar angle). Sample characterisation *in situ* was achieved by LEED and by soft-X-ray photoelectron spectroscopy (SXPS) using the incident synchrotron radiation. Both the wide-scan SXPS spectra for surface characterisation, and the narrow-scan O 1s spectra used in the PhD measurements, were obtained using an Omicron EA-125HR 125 mm mean radius hemispherical electrostatic analyser, equipped with seven-channeltron parallel detection, which was mounted at a fixed angle of 60° to the incident X-radiation in the same horizontal plane as that of the polarisation vector of the radiation.

A clean well-characterised rutile TiO_2(1 1 0) surface was prepared which gave a sharp (1 × 1) LEED pattern and a Ti 2p photoemission spectrum showing no significant high kinetic energy shoulder. The main Ti 2p peaks are generally assigned to Ti in the 4+ charge state expected for a fully ionic stoichiometric bulk site and in the autocompensated surface (e.g. [30]), while any high energy shoulder is assigned to Ti in a 3+ state, most commonly attributed to the presence of surface oxygen vacancies. To achieve this surface, the crystal was bombarded briefly with Ar^+ ions at an energy of 500 eV, followed by annealing in UHV at approximately 830 K.

The glycine powder was contained in a glass tube which could be heated via a surrounding copper coil and its temperature was measured by a thermocouple attached to a wire mesh within the tube. The doser was held within a small, separately pumped side-arm separated from the upper chamber by a gate valve, and was outgassed for prolonged periods (including between dosing) at ~370 K; line-of-sight dosing of the sample was conducted using a slightly higher doser temperature of 410 K for typically 60 s with the sample held at 200 K. The sample was then heated to room temperature and held at this temperature during all measurements.

3. Results

3.1. XPS characterisation

Fig. 2 shows the photoemission spectra in the energy range of the N 1s and O 1s peaks recorded at photon energies of 500 and 630 eV, respectively, following deposition at a sample temperature of ~215 K, and after annealing at ~325 K. A striking feature of the