



Pyrocatechol as a surface capping molecule on rutile TiO₂ (110)

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ABSTRACT

A 'cap and dip' method of adsorbing ruthenium di-2,2'-bipyridyl-4,4'-dicarboxylic acid diisocyanate (N3 dye) on a rutile TiO₂ (110) surface was investigated using pyrocatechol as a capping molecule. This method involves cleaning the rutile surface in ultra-high vacuum (UHV), depositing pyrocatechol onto the surface to 'cap' the adsorption sites, removing from vacuum, 'dipping' in an N3 dye solution and returning to vacuum. Photoemission measurements following the return of the crystal to vacuum suggest that the pyrocatechol keeps the surface free from contamination on exposure to atmosphere. Photoemission spectra also indicate that the pyrocatechol capping molecules are replaced by the N3 dye in solution and that the N3 dye is adsorbed intact on the rutile TiO₂ (110) surface. This technique may allow other large molecules, which are thermally unstable to evaporation in UHV, to be easily deposited onto TiO₂ surfaces.

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1. Introduction

TiO₂ is a wide-band-gap semiconductor used in many technological applications including photocatalysis, biomaterials and novel photovoltaic solar cells [1,2]. In the latter, TiO₂ is used in nanoparticulate form as an n-type semiconductor. However, TiO₂ absorbs light in the ultra-violet region of the electromagnetic spectrum so it must be modified for use in a solar cell. In the dye-sensitised solar cell, commonly known as the Grätzel cell, a dye is used to sensitize the TiO₂ to visible light [1]. The dye is excited by visible light and electrons are transferred into the conduction band of the TiO₂. The corresponding holes are transferred into the valence band of a p-type material.

The most efficient dye to date is ruthenium di-2,2'-bipyridyl-4,4'-dicarboxylic acid diisocyanate, also known as the N3 dye [3]. Fig. 1 (left) shows the N3 dye. It is composed of a central Ru atom, two bi-isonicotinic acid (BINA) ligands and two thiocyanate (N=C=S) ligands. The interface between the dye and TiO₂ has been the subject of many studies [4–7]. It is important to understand the adsorption geometry of the dye at the surface and the energy level alignment between the two materials since these influence the efficiency of the electron transfer across the interface, and hence the efficiency of the solar cell [6,7]. The anatase TiO₂ (101) is the surface that nanoparticles adopt so this is the most relevant surface to work with in single crystal form when carrying out surface science experiments in ultra-high vacuum (UHV). However, well-characterised single crystal anatase crystals are difficult to grow to sizes large enough for surface science experiments. The rutile

TiO₂ (110) surface is crystallographically equivalent to the anatase TiO₂ (101) (both cut along the longest diagonal of their respective unit cells) but high quality, well-characterised crystals are readily available so this surface has been widely studied [8]. The adsorption geometry of the BINA ligand affects the overall geometry of the N3 dye so the interaction of BINA with anatase and rutile TiO₂ surfaces has previously been studied [9–12]. It was found that BINA forms ordered layers up to several monolayers on the rutile TiO₂ (110) surface [10]. It is believed that the dye adsorbs to TiO₂ via the carboxyl groups of one BINA ligand [6,13] in a bridging bidentate geometry [10].

Most studies of the full N3 dye on TiO₂ adsorb the dye onto the surface *ex situ* [14–17]. This is because the dye cannot be evaporated in vacuum since when heated the dye decomposes before it evaporates. A technique called electrospray deposition has been developed to overcome this problem of depositing thermally unstable molecules. This technique sprays the molecules from atmosphere into 10^{−7}–10^{−9} mbar through several stages of differential pumping [18]. This means that the surface can be cleaned by sputter and annealing in vacuum to create a surface free from contamination [9]. Mayor et al. used the electrospray deposition technique to deposit the N3 dye onto a rutile TiO₂ (110) surface in vacuum [18]. They obtained results, which indicated that the dye was adsorbed to the TiO₂ surface intact.

Another method used for this purpose is a 'cap and dip' method. Here, the surface is cleaned in UHV so it is free from contaminants, then a small molecule (referred to hereafter as the capping molecule) which is easily evaporated in vacuum is deposited on the surface. The crystal is then removed from vacuum, and dipped in a solution containing the desired molecule. The basic idea is that the capping molecule is replaced by the molecule in solution whilst preventing atmospheric hydrocarbons from adsorbing on the surface [6]. When it is returned

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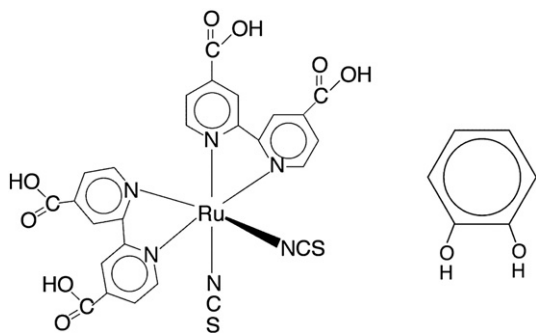


Fig. 1. The N3 dye (ruthenium di-2,2'-bipyridyl-4,4'-dicarboxylic acid diisocyanate) (left) and pyrocatechol (right).

to UHV the “target molecule” is now adsorbed on the surface in place of the capping molecule. The ‘cap and dip’ method may offer a more straightforward way of depositing thermally unstable molecules intact onto a surface in clean vacuum conditions. It also potentially allows vacuum-prepared dosed-surfaces to be studied under ambient atmospheric conditions.

In earlier work pivalic acid ($(\text{CH}_3)_3\text{CCOOH}$), known as trimethyl acetic acid was used to cap TiO_2 surfaces in UHV before removing from vacuum and substituting with a desired molecule from solution [6,19,20]. Pivalic acid adsorbs to TiO_2 via its carboxylic acid group following deprotonation to form pivalate, which scanning tunnelling microscopy (STM) measurements show stands perpendicular to the surface. Pivalic acid protects the adsorption sites at the surface from atmospheric contamination with its densely packed hydrocarbon chains. Here we propose a ‘cap and dip’ method using pyrocatechol (see Fig. 1 (right)) as the capping molecule. Pyrocatechol is thought to bind via its oxygen atoms to the TiO_2 surface following deprotonation. Near edge X-ray absorption fine structure (NEXAFS) [21] and STM measurements [22] have shown pyrocatechol forms an ordered monolayer on the rutile TiO_2 (110) surface. This may allow pyrocatechol to be displaced by the N3 dye (which bonds through carboxylic acid groups) more easily in solution than pivalic acid (which also bonds through carboxylic acid groups).

2. Material and methods

Experiments were carried out on beamline D1011 at MAX-lab, Sweden. Beamline D1011 is a bending magnet beamline with a photon flux of 10^{10} – 10^{11} photons s^{-1} . The base pressure of the main chamber was 5×10^{-10} mbar. The rutile TiO_2 (110) crystal (Pi-kem Ltd.) is cut and epi polished on one side to within 0.2° of the (110) plane. The crystal was prepared by repeated cycles of 1 keV Ar^+ ion etching and annealing to 750°C in vacuum until XPS spectra showed no contamination and a sharp (1×1) low energy electron diffraction (LEED) pattern was obtained [23]. Pyrocatechol powder was thoroughly degassed at room temperature under vacuum. It was evaporated into the chamber from a glass tube by gently heating the tube to -40°C . This results in saturation coverage of 1 monolayer (1 ML) [22].

Following photoemission measurements from the rutile TiO_2 (110) surface capped with pyrocatechol, it was removed from the UHV chamber via a ‘fast-entry lock’. A 0.5 mM N3-dye ethanolic solution [14] was dropped onto the sample and the sample was returned to the UHV chamber via the fast-entry lock. Total exposure to atmosphere was less than 2 min and the sample was returned to a vacuum of 2×10^{-7} mbar for approximately 5 min prior to being returned to the main chamber. Further photoemission spectra were then recorded.

Photoemission spectra were recorded at normal emission at a photon energy of 1000 eV. Spectra are aligned on the binding energy scale using Fermi edge scans recorded from the tantalum sample clips and binding energies are quoted to ± 0.1 eV. Peak fitting was

performed using CasaXPS software (copyright © 2005 Casa Software Ltd). A Shirley background [24] was subtracted from the data (which results in removal of noise outside the fitted region). Voigt curves (70% Gaussian:30% Lorentzian) were used to fit peaks to the spectra. These parameters were chosen as they gave a good fit to the experimental data.

3. Results and discussion

Photoemission spectra were recorded following the adsorption of pyrocatechol onto the rutile TiO_2 (110) surface in UHV. Fig. 2 shows the C 1s spectrum recorded from the pyrocatechol-dosed surface. Three peaks are fitted to the data at 284.3 eV, 285.6 eV and 289.0 eV. The peak at 284.3 eV is assigned to the 4 carbon atoms in the molecule that are in a C–C environment. The peak at 285.6 eV is assigned to the two carbon atoms in each molecule, which are in a C–O environment. The peak areas give approximately a 2:1 ratio as expected for the molecule. This suggests it is still intact on the surface. The small third peak at 289.0 eV is assigned to a π – π^* shake-up satellite feature [25].

The O 1s spectrum recorded from the pyrocatechol-dosed surface is fitted with two peaks as shown in Fig. 3(a). The peak at 530.3 eV binding energy (B.E.) is assigned to oxygen atoms in the TiO_2 surface [18,26]. The peak at 531.6 eV B.E. is assigned to oxygen atoms from the pyrocatechol [27] and the small feature at 533.7 eV is attributed to OH groups at the surface. It is not clear whether these peaks arise due to surface –OH groups or from a small number of pyrocatechol molecules where only one group is dissociated. These data are broadly in agreement with similar results for the adsorption of the related molecule dopamine on the anatase TiO_2 (101) surface [27]. The Ti 2p spectrum is fitted with four peaks as shown in Fig. 3(d). The peaks at 458.9 eV and 464.7 eV are assigned to titanium atoms in the Ti^{4+} state. These peaks arise from the 5-fold coordinated titanium atoms in the TiO_2 (110) surface [28]. The two peaks correspond to the $2p_{3/2}$ and $2p_{1/2}$ spin-orbit components respectively. The peaks fitted at 457.3 eV and 463.0 eV are assigned to titanium atoms in the Ti^{3+} state [23,29]. The Ti^{3+} peaks are small

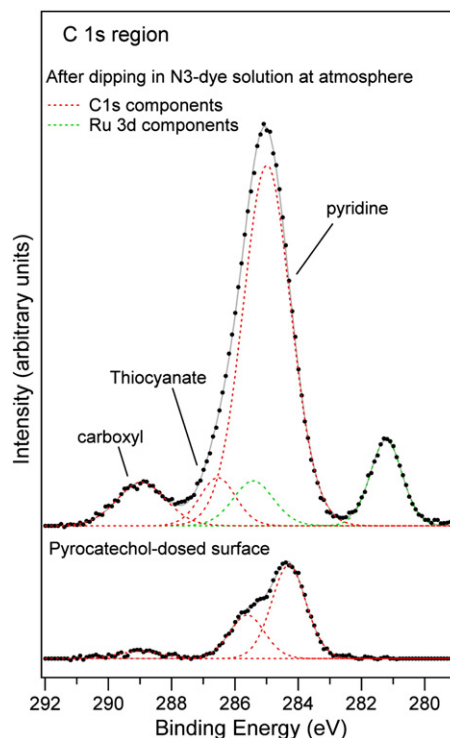


Fig. 2. C 1s photoemission spectrum of pyrocatechol adsorbed on rutile TiO_2 (110) and following ‘dipping’ of the capped surface in N3-dye solution at atmosphere.

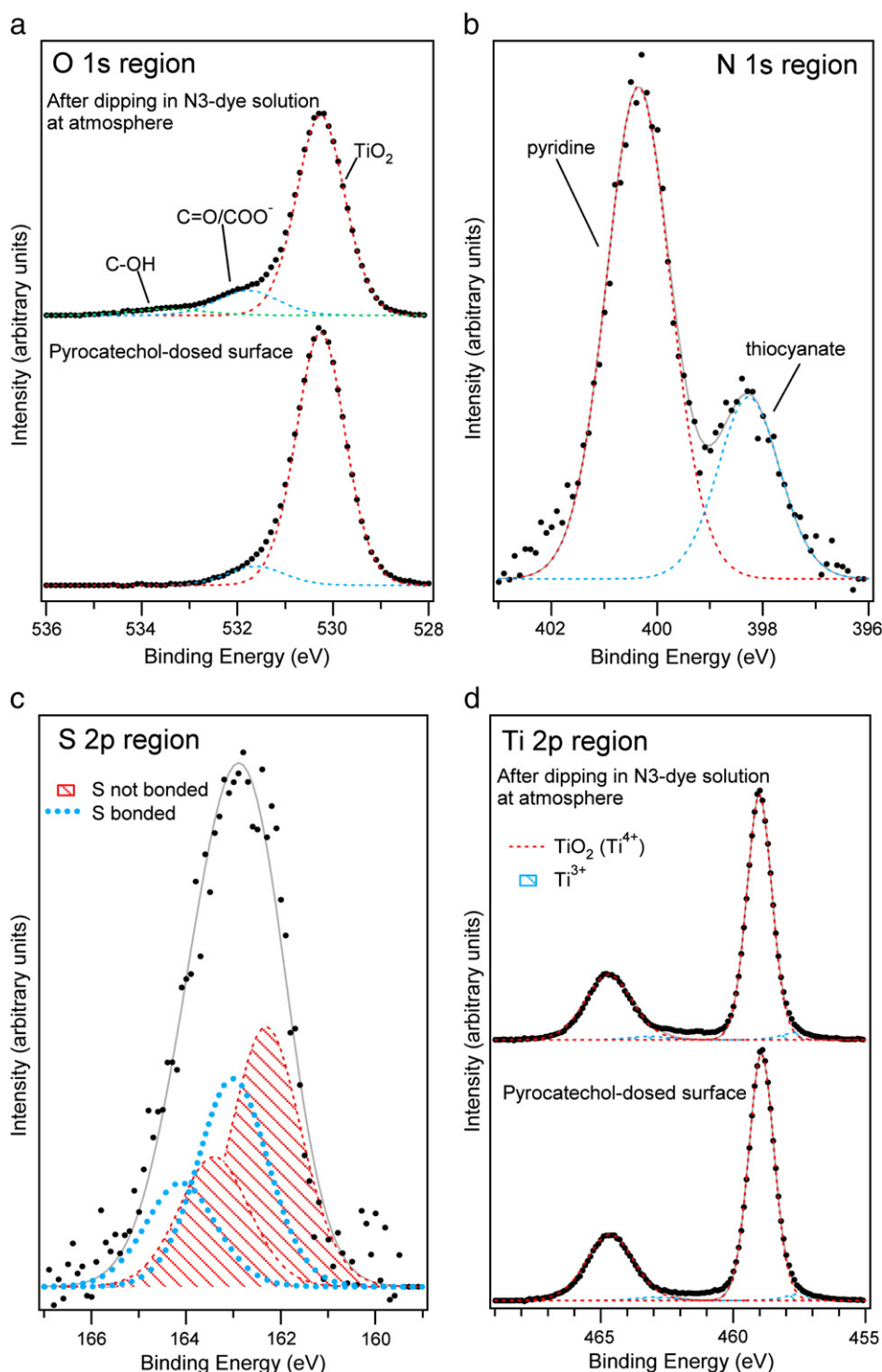


Fig. 3. Photoemission following 'dipping' of pyrocatechol-capped rutile TiO₂ (110) surface in N3-dye solution. (a) O 1s region (before and after dipping), (b) N 1s region, (c) S 2p region and (d) Ti 2p region (before and after dipping).

relative to the Ti⁴⁺ peaks, suggesting that there is a low Ti³⁺ concentration at the surface.

Fig. 2 shows the C 1s/Ru 3d spectrum following exposure of the pyrocatechol covered TiO₂ crystal to the ethanolic dye solution. The appearance of the Ru 3d_{5/2} and 3d_{3/2} spin-orbit-split peaks at 281.2 eV and 285.4 eV respectively indicate the presence of the N3 dye on the TiO₂ surface. The Ru 3d peaks were constrained to give the correct doublet separation [30] and theoretical intensity ratio. The C 1s components of the spectrum are fitted at 285.0 eV, 286.5 eV and 289.0 eV. Peak assignments are made by comparison with ref 25. The peak at 285.0 eV

is assigned to carbon atoms in the pyridine rings of the N3 dye (C–C). The peak at 286.5 eV is assigned to carbon atoms in the thiocyanate ligands of the dye (N=C=S). The peak at 289.0 eV is assigned to carboxyl atoms in the dye (COOH/COO⁻). Table 1 shows the ratio of areas of these three fitted peaks compared to the theoretical ratio expected for the intact N3 dye and the ratios found by the electrospray deposition method [18] of adsorbing the dye. This 'cap and dip' method using pyrocatechol agrees very well with the ratio found by electrospray deposition and that expected theoretically. Mayor et al. [18] explained the discrepancy between the intensity of their carboxyl signal with

Table 1

Ratios of fitted C 1s photoemission peaks assigned to pyridine, carboxyl and thiocyanate (for N3 dye on rutile TiO₂ (110) surface) using the pyrocatechol 'cap and dip' method and using the electrospray method [18] compared to theoretical ratio expected for the intact N3 dye molecule.

Ratio of C 1s chemical environments			
	Pyridine	Carboxyl	Thiocyanate
Theory	10	2	1
Electrospray [18]	10.2	1.2	1
'Cap and dip' using pyrocatechol	10	1.2	1

theoretical values by the fact that the carboxyl atoms are bonded to the TiO₂ surface, so electrons ejected from these 'buried' atoms may be more easily scattered. The good agreement of the 'clean and dip' measurements indicates that the dye is intact on the surface. It also suggests that the pyrocatechol has been displaced from the surface in the N3 dye solution, since the presence of pyrocatechol on the surface would skew the peak area ratio results. In addition, if it were not displaced it may not have allowed the dye to bond to the surface, since both molecules would be expected to bond to surface Ti sites.

Fig. 3(a) shows the O 1s spectrum following N3 adsorption using the 'cap and dip' method. The spectrum is fitted with three peaks at 530.3 eV, 531.8 eV and 533.5 eV. These are assigned to oxygen atoms in the TiO₂, C=O/COO[−] and C–OH environments respectively [18]. Carboxylic acids are thought to adsorb on the rutile TiO₂ (110) surface dissociatively *i.e.* they are deprotonated and adsorb as COO[−] [10,31]. Carboxyl groups not adsorbed to the surface give rise to two oxygen signals due to the chemical shift between C=O and C–OH groups [10]. Photoemission spectra recorded from electrospray deposited dye suggested that the dye adsorbs on the rutile TiO₂ (110) surface through two carboxyl groups on the same BINA ligand [18]. However, the STM measurements of Sasahara et al., who employed the cap and dip method using pivalic acid, suggested that adsorption is through two carboxyl groups from different BINA ligands [6]. In either case a ratio of 3:1 for C=O/COO[−]:C–OH environments would be expected. Table 2 shows that for the 'cap and dip' method employed in this work the ratio agrees very well at 3.2:1. This supports the suggestion that attachment of the dye is through two carboxyl groups although it is not possible to determine whether these groups lie on the same or different BINA ligands.

Fig. 3(b) shows the N 1s spectrum following N3 adsorption. The spectrum is fitted with two peaks at 398.3 eV and 400.4 eV. These peaks are assigned to nitrogen atoms in the thiocyanate ligands (N=C=S) and in the pyridine rings respectively [18]. In theory, there should be two pyridine nitrogen atoms for every thiocyanate nitrogen atom. Table 2 shows that the 'cap and dip' method gives a ratio of 2.8:1 which is in fairly good agreement with theory. The nitrogen spectra recorded here have a low signal/noise ratio so the

fitted peaks are likely to have a larger error in area associated with them.

The S 2p spectrum following adsorption of N3 dye is shown in Fig. 3(c). Similarly, the data has a low signal/noise ratio, making peak fitting more difficult. The spectrum was fitted with four peaks; two sets of spin-orbit doublets. The peaks at 162.3 eV and 163.4 eV are assigned to sulphur atoms not bonded to the surface (2p_{3/2} and 2p_{1/2} respectively). Following the assignment of Mayor et al. [18], the peaks at 163.0 eV and 164.1 eV are assigned to sulphur atoms which are bonded to the surface (2p_{3/2} and 2p_{1/2} respectively). Table 2 shows the ratio of the non-bonded and bonded peaks found by the 'cap and dip' method is 1.3:1 and that in theory the ratio expected for the N3 dye is 1:1. Again this discrepancy may lie in the fact that the "bonded" thiocyanate lies close to the surface and thus a proportion of the photoemitted electrons may be scattered by the main portion of the molecule above it [18]. Although the ratio of peak areas found here agrees reasonably with theory, it should be noted that the peak fitting for this spectrum was heavily constrained to give the correct S 2p spin-orbit splitting and to fix the FWHM of the doublets. We also note that it may be possible to fit the S 2p spectrum with a single doublet, therefore with these data it is not possible to conclude that the dye is bonded to the surface through the thiocyanate group. Hence, these data do not rule out bonding geometries suggested by other work [6] *i.e.* geometries where the thiocyanate group does not bond to the surface.

The Ti 2p spectrum following adsorption of the N3 dye is shown in Fig. 3(d) and is fitted with four peaks; two peaks at 459.0 eV and 464.7 eV assigned to titanium atoms in the Ti⁴⁺ state, and two peaks at 457.5 eV and 463.2 eV assigned to titanium atoms in the Ti³⁺ state. The relative peak areas of these fitted peaks have not changed significantly, following adsorption of the dye suggesting the dye has little or no effect on the surface Ti³⁺ concentration.

4. Conclusions

The 'cap and dip' method of depositing the N3 dye onto a rutile TiO₂ (110) surface using pyrocatechol as a capping molecule appears to have been successful. The good agreement of the photoemission data with theory and electrospray deposition data suggests that the N3 dye is adsorbed intact on the TiO₂ surface. The ratio of the O 1s fitted peaks agrees with the ratio expected for the molecule bonding to the surface through two carboxyl groups. The pyrocatechol molecules used to cap the surface prior to dipping in the N3 dye do not appear to give rise to a signal in the photoemission spectra, since a signal from the pyrocatechol would alter the peak area ratios from what is expected for the dye. This suggests pyrocatechol is replaced by the N3 dye in solution whilst at the same time helps to prevent adsorption of contaminants from the atmosphere on a short timescale. Other large molecules could potentially replace pyrocatechol at the TiO₂ surface allowing for deposition of other molecules via the same technique. In summary, the 'cap and dip' method using pyrocatechol as a capping molecule appears to be a viable and relatively easy method of adsorbing the N3 dye intact on a TiO₂ surface.

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Table 2

Ratios of fitted O 1s, N 1s and S 2p photoemission peaks for N3 dye adsorbed on rutile TiO₂ (110) surface, compared to theoretical ratios expected for the intact N3 dye molecule.

O 1s	C=O/COO [−]	C–OH
Theory	3	1
'Cap and dip' using pyrocatechol	3.2	1
N 1s	Pyridine	Thiocyanate
Theory	2	1
'Cap and dip' using pyrocatechol	2.8	1
S 2p	Non-bonded	Bonded
Theory	1.3	1
'Cap and dip' using pyrocatechol	1	1

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