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Molecular Adsorption and Charge Transfer Dynamics at Dye–TiO₂ Interfaces: An XPS, NEXAFS, and XSW Study

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*To my home KSA, my parents, my whole family, my
lovely small family (my husband and kids).*

Abstract

Dye-oxide interfaces provide a standard model system for investigating charge transfer, with dye-sensitised solar cell (DSSC) representing one of the most widely studied examples. Ruthenium dyes are among the most efficient sensitisers, as their electronic properties strongly favour binding to oxide surfaces in DSSC applications. N3 is one of the most extensively studied dyes, while D5 is an organic dye based on triphenylamine. In this thesis, these dyes are investigated on various titanium dioxide (TiO_2) surfaces. The primary objective of this study is to explore interfacial and surface chemistry central to DSSC operation, with a particular focus on the bonding and adsorption geometry of D5 and N3 on TiO_2 .

For sample preparation, D5 was deposited on single-crystal rutile $\text{TiO}_2(110)$ using electrostatic spray deposition (ESD) and on TiO_2 nanoparticles by drop-casting. In contrast, N3 was deposited on TiO_2 nanoparticles using ultra-high-vacuum electrospray deposition (UHV-ESD) to achieve the thinnest coverage, while drop-casting was used to obtain thin, medium, and thick films. The interfaces were characterised using X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure (NEXAFS), resonant photoemission spectroscopy (RPES), and normal-incidence X-ray standing wave (NIXSW).

Chapter 3 shows that the N3 dye, a ruthenium-based complex, is deposited onto $\text{TiO}_2(110)$ using an ultra-high-vacuum electrospray system and subsequently binds to $\text{TiO}_2(110)$, mesoporous TiO_2 , and TiO_2 nanoparticles primarily via carboxylic acid groups. In addition, hydrogen atoms from the carboxylic groups attach to bridging oxygen sites on the titanium surface. The sulphur atoms in the thiocyanate ligands exhibit multiple bonding configurations, interacting either with lattice oxygen on TiO_2 surfaces or directly with metallic substrates such as $\text{Au}(111)$ and Ti . N 1s NEXAFS measurements show that the LUMO and partial LUMO+1 lie within the band gap of mesoporous TiO_2 and TiO_2 nanoparticles, resulting in weak electronic coupling with the substrate. RPES reveals a reduced participant channel intensity, indicating rapid

charge transfer to the surface within the core-hole lifetime. Charge-transfer times from the LUMO+3 state are determined to be 3 ± 0.02 fs for bulk N3 at the thinnest coverage on TiO₂ nanoparticles, 10.9 ± 0.02 fs for thin N3 at thick coverage, and 18.7 ± 0.02 fs for monolayer and multilayer N3 on mesoporous TiO₂.

Chapter 4 provides a detailed investigation of D5 adsorbed on rutile TiO₂(110), mesoporous TiO₂, and TiO₂ nanoparticles using XPS, NEXAFS, and RPES. The results show that D5 bonds to TiO₂ via both the COOH group and C–OH hydrogen bonding. Hard X-ray photoelectron spectroscopy (HAXPS) reveals no significant difference in XPS peak intensities between monolayer and multilayer coverages, while the nitrile N≡C peak shifts to lower binding energy in multilayers. Measurements on TiO₂ nanoparticles exhibit similar bonding behaviour, except that complete deprotonation of C–OH occurs at thick coverage. Density functional theory (DFT) calculations support the observed electronic structure, with the HOMO localised on the triphenylamine unit and the LUMO on the thiophene group. The core-hole lifetime for LUMO+3 is calculated to be 0.5 fs.

Chapter 5 presents the adsorption geometry of N3 on rutile TiO₂(110) determined using the NIXSW technique. The vertical positions of selected atoms within N3, including the central ruthenium atom and carbon atoms in the carboxylate and thiocyanate groups, are measured relative to the TiO₂(110) surface. XPS identifies three components suitable for XSW analysis: Ru 3d_{5/2}, carbon in the COOH group, and carbon in the N=C=S group of thiocyanate. Analysis of the TiO₂(220) reflection shows that the Ru atom is located at the centre of the molecule, 8.3 ± 0.07 Å above the TiO₂(110) surface, corresponding to a position between the fourth and fifth lattice planes ($n = 4-5$). Both carboxylic and thiocyanate groups exhibit two distinct height environments. The carboxylic groups display a low-lying component at 2.8 ± 0.12 Å, consistent with 2-M bidentate bonding in which each carboxylate bridges two surface Ti atoms, together with higher components at $n = 6$ and $n = 8$ above the Ru centre. The thiocyanate groups are located at $n = 4$ (7.7 ± 0.11 Å) below Ru and at $n = 6$ (10.8 ± 0.11 Å) above Ru. These results confirm that Ru occupies

a central position within N3 and that N3 anchors to $\text{TiO}_2(110)$ predominantly via a 2-M bidentate geometry, in good agreement with DFT predictions.

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List of Publications

1. A soft X-ray probe of N3 sensitized titanium dioxide nanoparticles.
Mashael M. Alotaibi,^{a,b†} Jack Hart^a Eleanor Frampton^a James N.O'shea,^{*a}
(under preparation)
2. The X-ray Photoemission and Near Edge X-ray spectroscopy and Resonant photoemission spectroscopy of Triphenylamine on TiO₂ NanoParticles.
Mashael M. Alotaibi,^{a,b} James N.O'shea,^{*a} (under preparation)
3. Adsorption Geometry of N3 Dye on Single Rutile TiO₂(110) Surface Investigated by NIXSW Technique
Mashael M. Alotaibi,^{a,b} Abdulrahman Alotaibi^a Tyler James^a David Duncan^a
James N.O'shea,^{*a} (under preparation)

List of Abbreviations

DSSCs	Dye-Sensitised Solar Cells
UHV	Ultra-High Vacuum
STM	Scanning Tunnelling Microscopy
XPS	X-ray Photoelectron Spectroscopy
NEXAFS	Near-Edge X-ray Absorption Spectroscopy
RPES	Resonant Photoelectron Spectroscopy
NIXSW	Normal Incident X-standing Wave
NPs	Nano Particles
DoS	Density of State
GL	Gaussian and a Lorentzian
IMFP	the inelastic mean free path
XAS	X-ray Absorption Spectroscopy
MCP	microchannel plate
CHCS	Core-hole Clock Spectroscopy
ESD	Electrospray Deposition
NE	normal emission
PE	Photon Energy
BE	Binding Energy
SMS	Surface and Material Science
PEY	partial electron yield
PES	photoelectron spectroscopy
TPA	Triphenylamine
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Occupied Molecular Orbital
VB	Valence Band
F_c	Coherent Fraction
P_c	Coherent Position

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Chapter 1

Introduction

1.1 Introduction

Fossil fuels currently supply most of the energy and chemical products needed by a growing population. However, excessive use of fossil fuels contributes to air and water pollution and is a major driver of climate change [1]. Renewable energy offers a promising solution to these issues [2]. Solar energy stands out for its widespread availability and sustainability. Solar cells utilise the photovoltaic effect to convert sunlight into electricity, making them a crucial technology for energy harvesting [3]. In addition to water splitting, sensors, and photocatalysis, dye-sensitised solar cells (DSSCs) are an important application in which dye molecules are used to convert sunlight into electricity [4]. After a DSSC absorbs light, the most challenging part is determining what happens to the charge (electrons and holes). When a substance absorbs a photon, an electron is excited, leaving behind a hole. These charges must be transferred to an interface where they can be put to good use, such as generating electricity or initiating a chemical reaction. If they recombine before reaching the interface, the energy is lost. This means that the device's overall success often depends on how well charge can pass across the interface. Several factors influence interfacial charge transport in DSSCs, including bonding and

geometry.

In DSSCs, this charge-transfer process involves, firstly, the bonding of the dye molecule to the oxidised surface via carboxylate or isocyanate groups, thereby directly influencing the electronic overlap and the arrangement of molecular orbitals relative to the oxidised orbitals. Strong coupling and optimal geometry enhance the overlap between the dye orbitals and the oxide substrate. This facilitates charge transfer by shortening the distance between the donor and acceptor and strengthening the electronic coupling [5]. Secondly, energy alignment, which means aligning energy for efficient electron injection from an excited dye into the oxide. The energy levels must be aligned in a way that the dye’s lowest unoccupied molecular orbital (LUMO) has more energy than the conduction band edge of the oxide [6, 7]. This facilitates the transfer of photo-generated electrons. They move preferentially from the excited dye’s LUMO into the TiO_2 conduction band, facilitating efficient charge transport. The anchoring group and the surrounding environment (such as solvent and co-adsorbents) can influence these energy levels. This influences the total injection rates and directionality. In dyes such as N3, this energy level alignment enables fast electron injection into the TiO_2 conduction band. [5]. Thirdly, the timescale describes the competition between ultrafast electron transfer from the excited dye into the oxide and recombination processes, which occur on femtosecond to picosecond timescales. This electron injection occurs much faster than recombination processes, which return the excited electron to the ground state. Therefore, sustaining rapid injection kinetics via structural and energetic regulation is crucial for achieving high device efficiencies [8]. All three factors—molecular bonding, energy alignment, and transfer timescale must be adjusted together to facilitate efficient charge separation and reduce recombination at hybrid interfaces in solar energy and photo-catalytic applications [9].

These factors are interconnected, and their simultaneous optimisation leads to improved device performance. Ultrafast spectroscopic studies show that dyes often inject electrons into TiO_2 in less than ten to one hundred femtoseconds [10]. Recombination, on the other hand, occurs more slowly (nanoseconds to milliseconds), so fast injection is possible if the interfacial contact is strong. Here, recombination refers to interfacial charge recombination between electrons injected into TiO_2 and the oxidised dye molecules. Researchers have found that modifying surfaces, such as combining semiconductors or incorporating carbon nanostructures, can facilitate charge separation [11]. One of the most significant challenges in photonic science is understanding and controlling charge transfer at interfaces. Reactions between dyes and oxides can serve as a model to learn more about this phenomenon. In these systems, the dye molecule transfers charge across a phase boundary to the much larger oxide. This size difference reduces the probability of electrons returning to the dye after injection, thereby improving charge separation and reducing recombination.

1.2 Dye-Oxide interfaces

Dye-oxide interfaces provide a common model system for investigating charge transfer. The most representative model of dye-oxide systems is the dye-sensitised solar cell (DSSC) [12], which was first reported by Brian O'Regan and Michael Grätzel in 1991. They used a colloidal solution of TiO_2 sheets to produce TiO_2 electrodes [12–14]. These devices have attracted significant interest due to their ability to convert solar energy into chemical energy directly and still exhibit several desirable features, including affordability, attractive designs, enhanced power conversion efficiency, ease of manufacture, flexibility, and semi-transparency [13, 15–17]. The working principle of DSSCs is shown in Figure 1.1 where the dye (D5) molecule absorbs the light. The electron is excited from the molecule's highest occupied molecular orbital (HOMO) to its lowest unoccupied molecular orbital (LUMO) as shown in Fig 1.1 (a). The

excited electron is injected into the conduction band of TiO_2 (b). The electron is then transported through the TiO_2 network to the counter as (c). Finally, the redox couple donates an electron to regenerate the dye (e) [14, 18, 19].

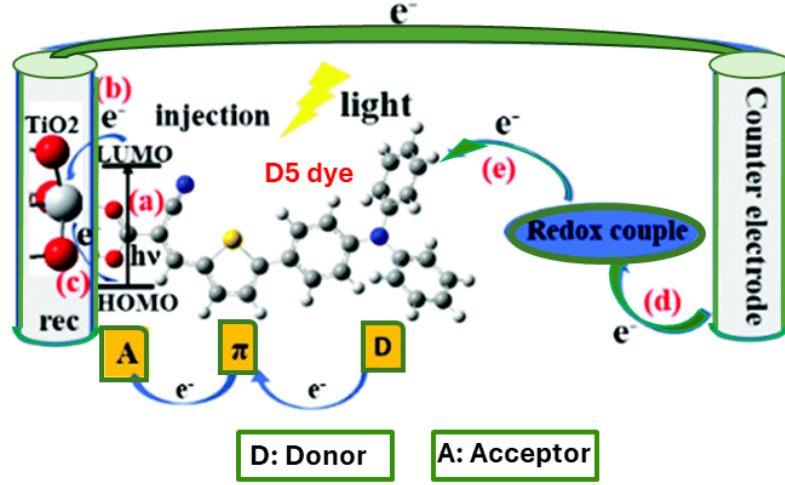


Figure 1.1: Schematic illustration of the working principle of a dye-sensitized solar cell (DSSC). (a) Photo-excitation of the dye molecule from the HOMO to the LUMO. (b) Electron injection from the excited dye into the TiO_2 conduction band. (c) Transport of electrons through the TiO_2 and the external circuit to the counter electrode. (d) Regeneration of the oxidised dye by electron donation from the redox couple. (e) Reduction of the redox couple at the counter electrode, completing the electrical circuit [20].

The structure of the D5 molecule is shown in Figure 1.1, which features a triphenylamine (TPA) group as an electron donor and a cyanoacrylic acid group as an electron acceptor. These groups are connected via a π -conjugated system [21]. The cyanoacrylic acid group also anchors the molecule to the TiO_2 surface through deprotonation of the carboxylic acid, as shown by a recent study [22]. One of the most extensively studied dyes is N3 (Ru 535); its structure is *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium (II) (N3) as shown in Figure 1.2.

Nazeeruddin and co-workers first reported the N3 dye in 1993 [23]. It has since been studied on various substrates, including ZnO [10] and different forms of TiO_2 such as single-crystal rutile $\text{TiO}_2(110)$ [24]. More recently, N3

has also been investigated on mesoporous TiO_2 [25] and aluminium oxide [26]. The bi-isonicotinic acid is a part of the N3 molecule, as shown in Figure 1.2. Studies on the bi-isonicotinic acid ligand, deposited using ultra-high-vacuum (UHV) techniques, predate these investigations. The studies employed a rutile $\text{TiO}_2(110)$ single-crystal surface [27, 28] and anatase TiO_2 nanoparticles [29] to determine the molecular bonding geometry to the TiO_2 surface. While researchers have studied different dyes on TiO_2 to investigate the bonding and geometry, such as L0 dye [30], and D5, SC4, R6 [22]. Whereas N3 dye adsorption on $\text{Au}(111)$ has been reported in [31].

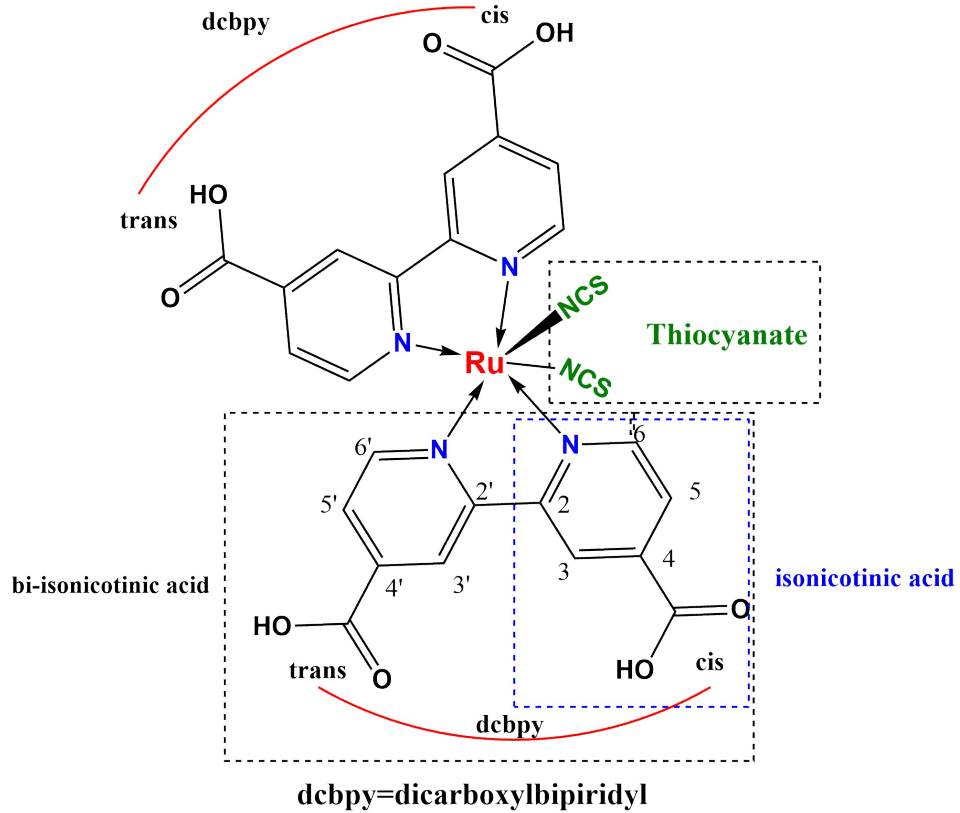


Figure 1.2: Schematic of N3 dye molecular. The structure is cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium (II). It contains a metal-organic in the centre of the molecular Ru, two thiocyanate $\text{N}=\text{C}=\text{S}$, and two bi-isonicotinic acids.

1.3 TiO_2 forms

Titanium dioxide TiO_2 plays a significant role in diverse applications, including photovoltaic, catalysis, and sensors [32]. Figure 1.3 displays TiO_2 forms, such as anatase and rutile, along the (110) direction, and also includes mesoporous and TiO_2 nanoparticles [33]. The rutile (110) surface is the most commonly used because it is more stable and has been intensively studied in the context of DSSCs [22, 24, 25]. Mesoporous TiO_2 is also a promising material for photo-catalytic applications, as it can significantly enhance photo-catalytic performance compared to commercially available options. TiO_2 nanoparticles are highly effective in dye-sensitised solar cells; their size range of 1–100 nm provides a high surface area, facilitating dye loading and reducing recombination. This work will focus on TiO_2 and on how dye molecules bind to the nanoparticles' surfaces.

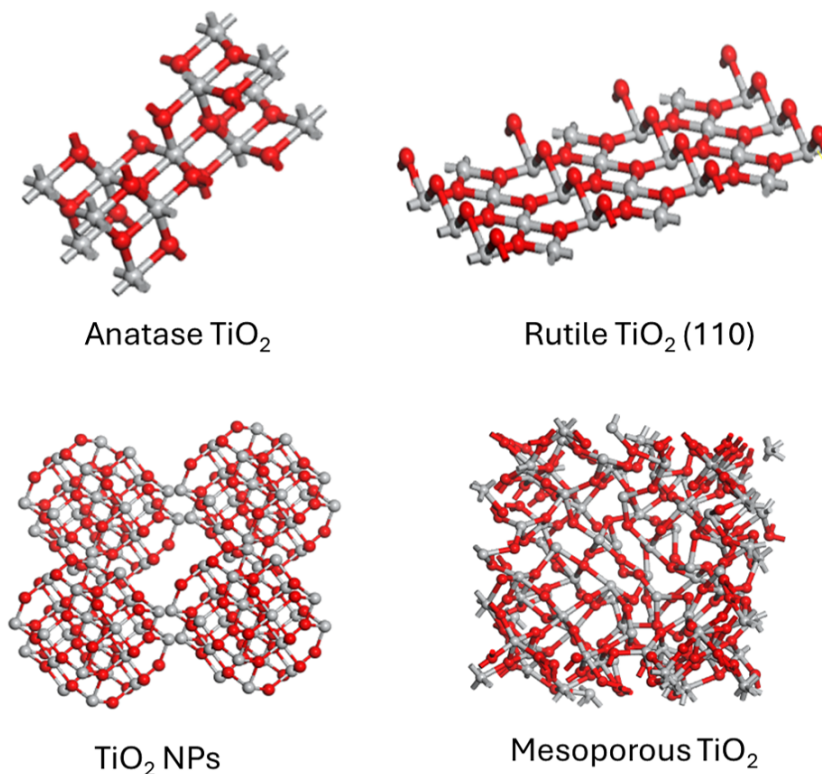


Figure 1.3: TiO_2 exists in several forms, including rutile (110), anatase, mesoporous structures, and nanoparticles.

1.4 How does dye anchor to TiO_2 ?

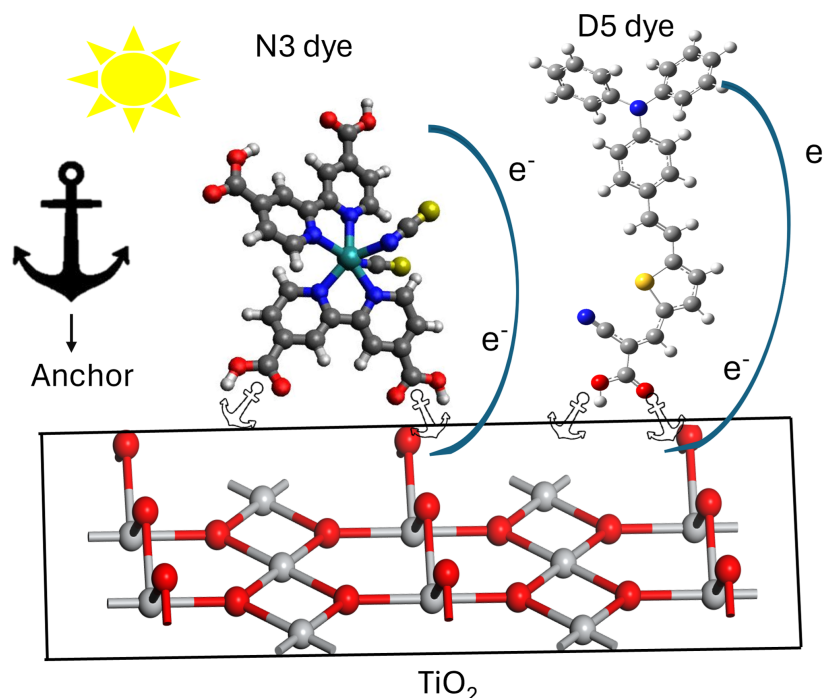


Figure 1.4: Schematic diagram of adsorption of N3 and D5 on a TiO_2 surface. TiO_2 .

In the previous section, interfaces were introduced, and the adsorption of the dye on the TiO_2 semiconductor was discussed. This section discusses in more detail how the dye anchors to TiO_2 . The word "anchors" indicates chemical groups that facilitate attaching dye molecules to the surface of a material, in this case, titanium dioxide TiO_2 . The most common in chemical groups are carboxylic acid ($-\text{COOH}$) and cyanoacrylic acid ($-\text{CH}=\text{C}(\text{CN})(\text{COOH})$) [34–38]. Figure 1.4 presents a schematic of N3 and D5 dyes adsorbed on a TiO_2 substrate, highlighting the binding of the carboxylate (COOH) groups to the TiO_2 surface. Carboxylic acid and cyanoacrylic acid were chosen because they form strong covalent bonds with TiO_2 and act as electron-withdrawing groups, which support electron injection from the dye into TiO_2 . Their well-studied binding modes, as shown in Figure 1.5, for example, monodentate, bidentate

chelating, or bridging– known to provide both stability and efficient charge transfer, further enhance the overall dye- TiO₂ interaction.

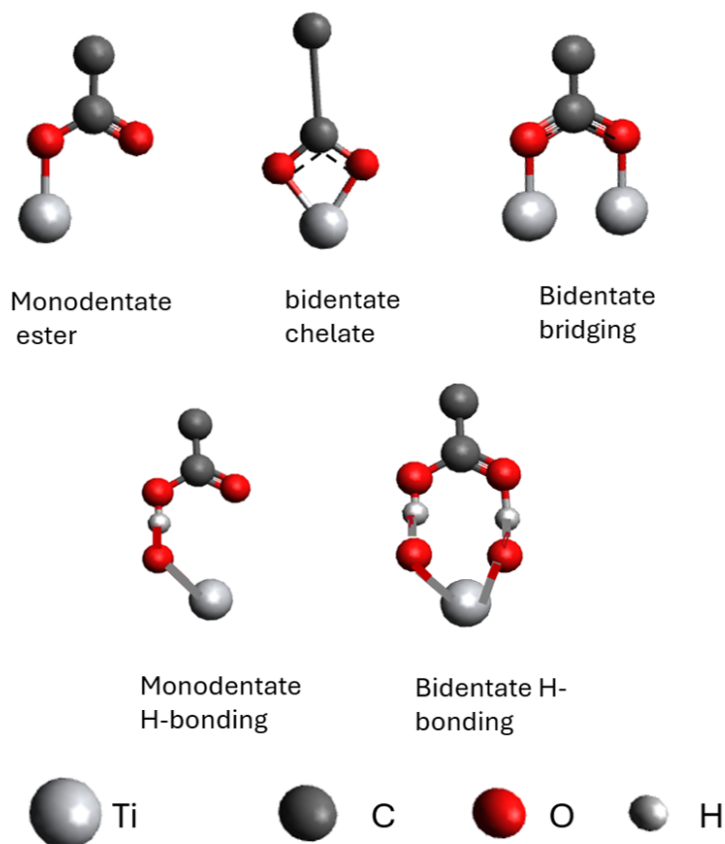


Figure 1.5: Different binding modes for carboxylic acid may bind to a metal oxide such as TiO₂, carboxylic acid groups of bi-isonicotinic acid ligands, and the sulphur atom of thiocyanate ligands.

1.5 Adsorption geometries of N3 on TiO₂

Bi-isonicotinic acid on rutile TiO₂(110) adopts a 2-M bidentate bonding geometry via deprotonation [27, 28]. In contrast, for adsorption on the anatase TiO₂(110) surface, bi-isonicotinic acid is bonded in a similar manner, although with significantly different adsorption geometries [29]. It is also, of course, important to understand how N3 interacts with TiO₂. O’Shea et al found that carboxylic acid groups of bi-isonicotinic acid ligands and the sulphur atom of thiocyanate ligands both facilitate attachment to TiO₂ [24] as shown in Figure 1.6(a). However, Wayment-Steele et al have proposed that the N3 bonds to

TiO₂ through carboxylic acid groups without the involvement of the sulphur atom of thiocyanate [39].

Ben Manaa et al. have studied the adsorption of the N3 dye on mesoporous TiO₂. They found that it binds via multiple modes, including monodentate via an H-bond and bidentate via an H-bond [40]. More recently, studies on mesoporous TiO₂ found that it binds via a mixture of bidentate and monodentate geometries [25], consistent with the previous study. In addition, Kley's group studied N3 on TiO₂ anatase (101), reporting multiple binding configurations [41]. While carboxylic acid groups bond with aluminium oxide layers [26]. In contrast, sulphur thiocyanate ligands bind to Au surfaces [31]. However, another study reported possible adsorption modes of N3 on Au(111), Figure 1.6(b). In isolated bi-isonicotinic ligands, a flat configuration is observed, whereas N3 shows a tilted adsorption geometry with additional sulphur bonding via thiocyanate [42]. These studies demonstrate that N3 exhibits different anchoring modes on rutile and mesoporous TiO₂ surfaces. However, it remains unclear whether N3 adsorption on TiO₂ nanoparticles follows similar binding configurations. At the nanoscale, particle curvature and reduced dimensions may influence the adsorption geometry and anchoring of N3 through its carboxylic groups. Therefore, the basic binding approach will remain the same, but could be slightly different, making the interaction of N3 on NPs a subject to explore.

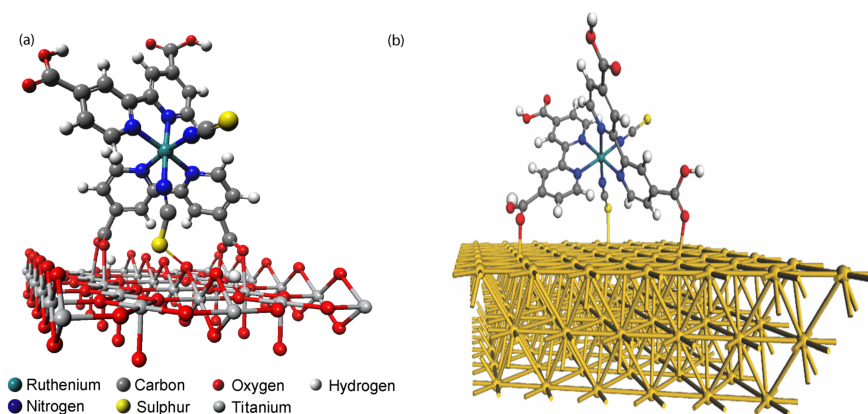


Figure 1.6: (a) N3 adsorbed on rutile $\text{TiO}_2(110)$, illustrating binding via the carboxylic acid groups of the bi-isonicotinic acid ligands and the sulphur atom of the thiocyanate ligands (adapted from Ref [24]. (b) N3 adsorbed on $\text{Au}(111)$, showing a different adsorption configuration[42]

1.6 Adsorption geometries of D5 on TiO_2

In the preceding section, we described how the N3 dye bonds to TiO_2 through anchors and its adsorption geometry. In this section, we discuss what researchers have found about D5 on TiO_2 . The adsorption of D5 on nanoporous anatase TiO_2 has been studied by Hahlin et al [43]. They found that the anchoring group is cyanoacrylic acid, with a bidentate and bridging binding mode. A recent study investigated D5 on rutile $\text{TiO}_2(110)$ and found that the cyanoacrylic acid moiety, acting as the anchoring ligand, forms a bidentate coordination [22]. The L0 dye exhibits similar adsorption behaviour to D5 due to the presence of the same cyanoacrylic acid anchoring group.

Researchers have suggested a mixture of bidentate-bridging and possibly monodentate or physisorbed geometries [30]. To date, no study has shown D5 bonding to TiO_2 nanoparticles. This makes our work particularly interesting and allows comparison with previous studies. Due to its substantial and fragile structure, non-volatility, and thermal lability, N3 cannot be deposited by traditional evaporation. This limitation led to the use of electrospray deposition,

a technique discussed in Chapter 2. Many studies have explored various dyes for TiO_2 to achieve efficient DSSCs. These include N3 [24], L0 dye [30], D5, SC4, and R6 [22]. Kley et al. used electrospray in UHV to deposit N3 molecule on TiO_2 anatase (101). Scanning tunnelling microscopy (STM) revealed several adsorption geometries, including monodentate, bidentate bridging, and bidentate chelating modes via carboxylic acid groups. Supramolecular interactions, such as hydrogen bonding between adjacent dye molecules, also contribute [41]. Researchers used many techniques, such as X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption spectroscopy (NEXAFS), and resonant photoelectron spectroscopy (RPES) on many dyes, including N3 and D5 [14, 22, 24, 25, 30, 31, 44, 45].

To date, however, the normal-incidence X-ray standing wave (NIXSW) technique has not been applied to the N3/ TiO_2 system.

1.7 Topics researched in this thesis

This thesis aimed to explore the interface in DSSCs, focusing on bonding and geometry between the dyes (D5 and N3) and TiO_2 NPs. The charge-transfer time is then determined using the core-hole clock technique. These results will be compared to earlier studies on single-crystal $\text{TiO}_2(110)$ [24] and mesoporous TiO_2 [25]. The next chapter continues the study of N3 by applying the NIXSW technique to analyse N3 on $\text{TiO}_2(110)$. This will reveal the location of the central atom in the N3 molecule: the Ru atom on the surface. The thesis structure is as follows:

Chapter 1 addresses the study of the dye-oxide interface, focusing on how dyes anchor to TiO_2 . It reviews key literature on the adsorption of D5 and N3 dyes on oxides, as well as the deposition methods and analytical techniques applied to these dyes.

Chapter 2 This chapter presents the essential methods for experiments and relevant background information, including X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption spectroscopy (NEXAFS), resonant photoelectron spectroscopy (RPES), core-hole clock, and electrospray deposition (ESD). Synchrotron radiation and two types of X-ray sources: soft and hard. Finally, the Normal Incidence X-ray Standing Wave (NIXSW) technique, together with Density Functional Theory (DFT) calculations, was employed to support the experimental findings and elucidate the adsorption characteristics on TiO_2 surfaces.

Chapter 3 presents the results of N3 dye adsorption on various TiO_2 structures, including single crystals (110), mesoporous frameworks, and nanoparticles using XPS, NEXAFS, and RPES techniques. These methods, described in Chapter 2, enabled detailed analysis of binding configurations and adsorption geometry.

These results are compared with N3 on TiO_2 single crystals (110) and mesoporous structures.

Chapter 4 This chapter presents the results of the D5 dye adsorption study on various types of TiO_2 , including single crystals, mesoporous structures, and nanoparticles. The analysis was conducted using XPS, NEXAFS, and RPES, following the experimental methods described in Chapter 2. This approach ensures continuity with previous chapters and enables direct comparison across different TiO_2 morphologies.”

Chapter 5 This chapter presents detailed results of N3 dye adsorption on $\text{TiO}_2(110)$, obtained using the Normal Incidence X-ray Standing Wave (NIXSW) technique at the (220) reflection. This builds on previous N3 studies by incorporating refined experimental insights into adsorption geometry and vertical bonding configuration.

Chapter 6 presents a structured summary of the research conducted for this thesis, offering recommendations for future work that tie together the core findings and implications from all prior chapters.

Chapter 2

Experimental Methods

2.1 X-ray Photoelectron Spectroscopy

2.1.1 Technique

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive technique that provides quantitative information on the elemental composition and chemical states of a material by analysing photoelectrons emitted via the photoelectric effect, in which an incoming photon has sufficient energy to ionise the material being examined. The binding energy of the photoelectron prior to ionisation can be determined from energy conservation using the measured kinetic energy. It should be noted that the relevant work function in 2.1 is that of the analyser, as the measured kinetic energy is referenced to its Fermi level.

$$h\nu = E_B + E_{ks} + \phi_s \quad (2.1a)$$

$$E_B = h\nu - E_{ks} - \phi_s \quad (2.1b)$$

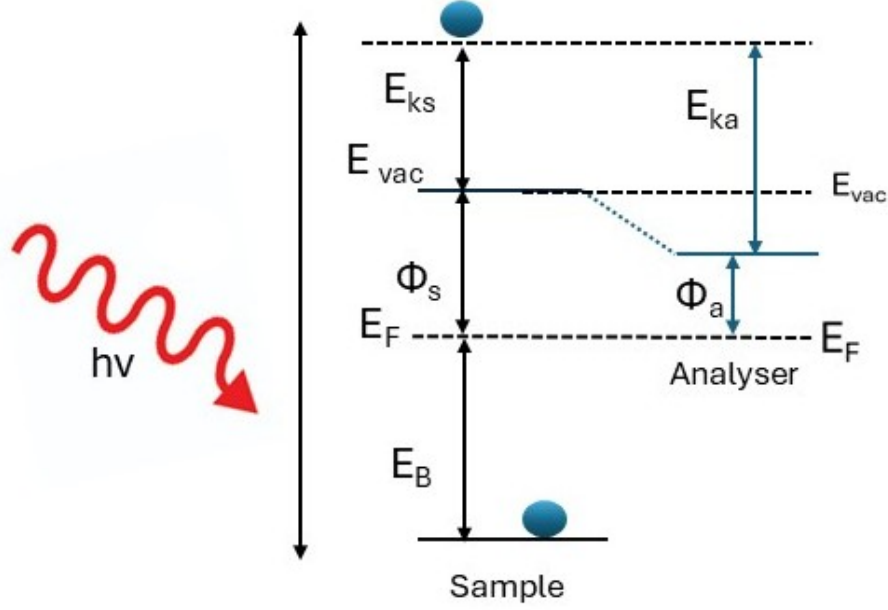


Figure 2.1: Schematic illustration of the basic principle of X-ray photoelectron spectroscopy (XPS). The photoemission process is commonly described using a three-step model: photoexcitation, transport of the electron to the surface, and escape into vacuum. The kinetic energy of the emitted electron is determined by the photon energy, the binding energy, and the work function. In this context, the subscript ‘s’ signifies the sample, while ‘a’ represents the analyser.

where $h\nu$ represents the photon energy, E_B denotes the binding energy, E_{ks} signifies the kinetic energy, and ϕ_s indicates the work function of the sample. This relationship is illustrated in Figure 2.1. Nonetheless, the kinetic energy of the photoelectron must be quantified, and the analyser possesses its own work function ϕ_a , as shown in Figure 2.1. Depending on the relative magnitude of ϕ_s compared to ϕ_a , the electrons either accelerate or decelerate upon detection by the analyser (the former case is illustrated in Figure 2.1). Consequently, following measurement, Equation (2.1b) is transformed into:

$$E_B = h\nu - E_{ka} - \phi_s + (\phi_s - \phi_a) \quad (2.2a)$$

$$E_B = h\nu - E_{ka} - \phi_a \quad (2.2b)$$

Figure 2.1 illustrates the energy relationships underlying Equation (2.2a), with each term corresponding to the photon energy and the associated energy levels involved in the XPS process. The sample work function is not necessary for measuring the kinetic energy of photoelectrons; only the analyser's work function is required. Consequently, ϕ_a can be taken as a correction and is a known variable, facilitating the computation of E_B . Binding energy is influenced by the electron's chemical surroundings in the initial state, making XPS a direct probe of both chemical and electronic information.

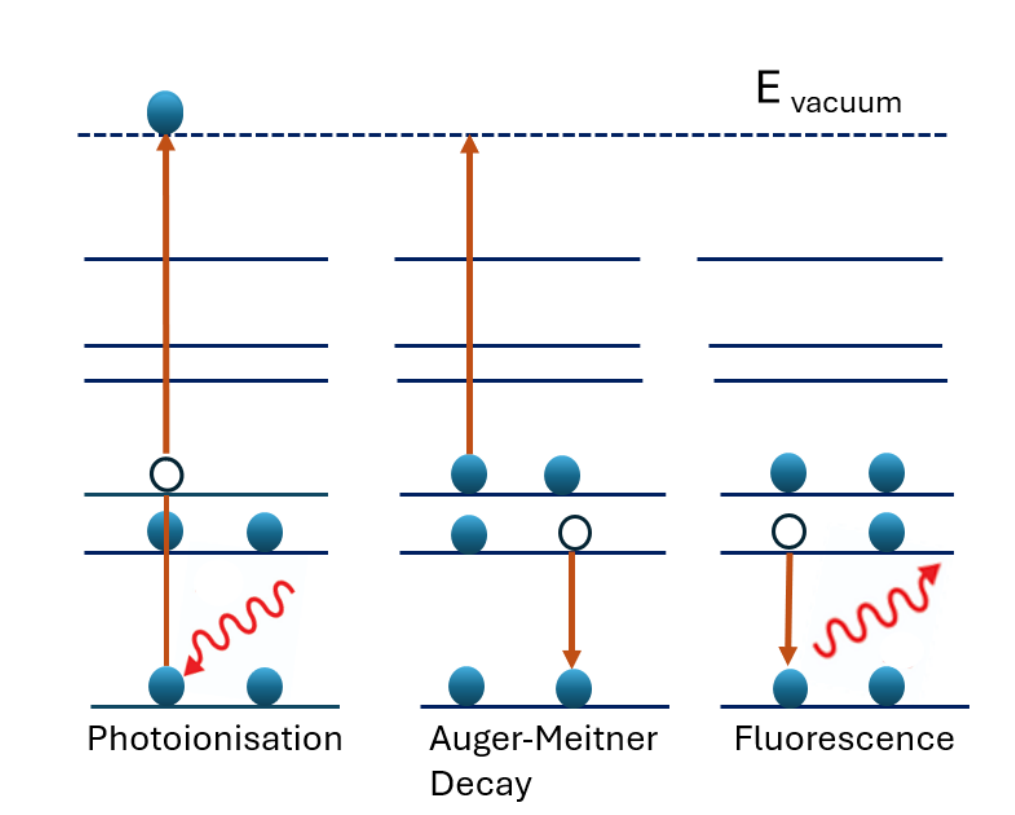


Figure 2.2: Energy level diagrams of XPS show the relaxation processes that occur following ionisation: Auger-Meitner decay (non-radiative) and fluorescence (radiative).

During photoionisation, the sample is placed in an excited state. This is unstable and will eventually decay. The core-excited state might appear in one of two ways, as seen in Figure 2.2. Both Auger-Meitner decay and fluorescence initiate similarly: an electron from a higher energy level fills the core hole. In Auger-Meitner decay, this process is accompanied by the autoionisation of an-

other electron, but in fluorescence, a photon is emitted. X-ray photoelectron spectroscopy (XPS) is a photon-in, electron-out technique that lacks sensitivity to fluorescence. Nonetheless, Auger-Meitner electrons can be identified and frequently manifest in spectra.

The primary distinction between Auger and photoelectron peaks in the recorded spectrum is in their response to increasing photon energy. As photon energy escalates, the kinetic energy of the photoelectron correspondingly increases, but E_B remains constant according to Equation (2.2a). Conversely, for Auger-Meitner electrons, an increase in photon energy does not enhance their kinetic energy. The kinetic energy of the Auger-Meitner electron is derived from the energy difference between the core-excited and ground states, rather than the photon, resulting in a shift of Auger-Meitner peaks on the binding energy scale.

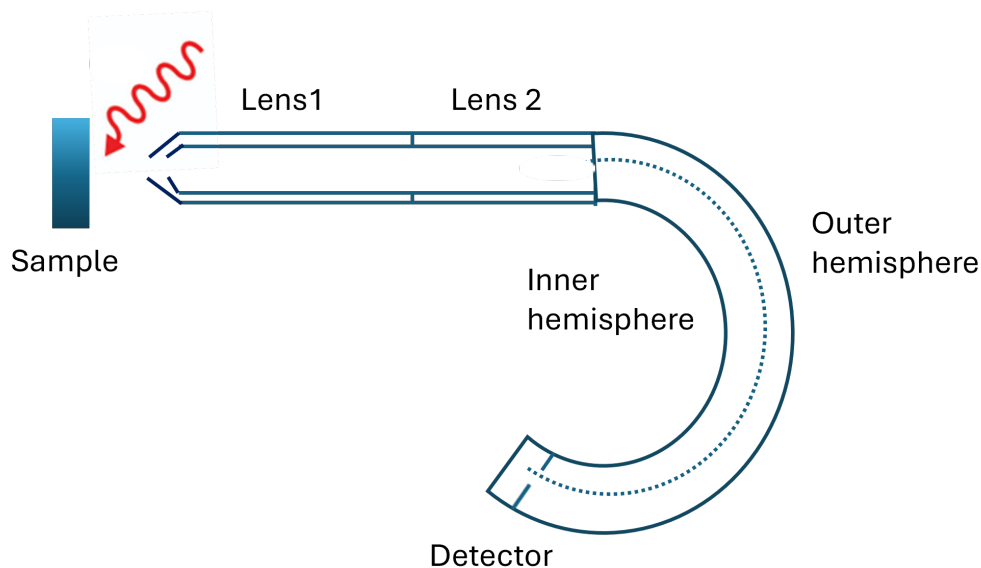


Figure 2.3: A diagram of a hemispherical analyser utilised to determine the kinetic energy of photoelectrons. The photoelectrons are concentrated and decelerated by an electrostatic lens mechanism before entering the hemisphere.

XPS often utilises hemispherical analysers to assess the kinetic energy of photoelectrons. The operational principle of this electron analyser is illustrated in Figure 2.3. The sample receives radiation, resulting in the emission of photoelectrons from many energy levels, with their kinetic energy determined by

Equation (2.2a). The electrons thereafter enter the hemispherical analyser after being focused and decelerated by two electrostatic lens devices.

The preceding lens is crucial as it enables electrons entering the analyser to reach the slit of the hemisphere. The latter, due to the frequently increased kinetic energy of the photoelectrons, limits sufficient resolution [45]. Only electrons with kinetic energies matching the analyser pass energy are transmitted to the detector, as defined by

$$E = ke\Delta V \quad (2.3)$$

where E represents the energy associated with the dashed line shown in Figure 2.3 "e" denotes the elementary charge, ΔV signifies the potential difference between the hemispheres, and k is the spectrometer constant determined by the inner and outer radius of the hemisphere [45]. Electrons entering the analyser with excessive or insufficient energy will thus remain unmeasured. Hemispherical analysers may be used in many modes to record a spectrum. However, the only mode relevant to this thesis is constant analyser energy (CAE). This functions by setting a 'pass energy' that defines the path the photoelectrons must travel to reach the detector. The lens system accelerates or slows the electrons to this energy with a variable voltage that selects the recorded kinetic energies, enabling the hemispherical analyser to quantify the intensity of photoelectrons as a function of kinetic energy. The selection of pass energy primarily relies on the context, as a trade-off exists between intensity and resolution. Higher pass energies yield greater intensities relative to lower values, although at the expense of resolution, and conversely.

The phenomenon arises from the energy separation of photoelectrons as they pass the hemisphere; at high pass energies, small shifts in kinetic energy are directed to analogous locations on the detector, thereby diminishing resolution

while increasing intensity. In addition to the pass energy, the entrance slit of the analyser also contributes to determining the resolution. The greater its dimension, the more electrons pass the hemisphere and can access the detector; however, resolution is compromised once more. The energy resolution of XPS is determined by

$$\Delta E = E_p \left(\frac{W}{2R} + \frac{\alpha^2}{2} \right) \quad (2.4)$$

where ΔE denotes the resolution, E_p represents the pass energy, W indicates the entry slit width, R signifies the radius of the path defined by E_p , and α refers to the angle at which the photoelectrons enter the hemisphere [45].

2.1.2 Processing

As with many spectroscopies, XPS spectra cannot be interpreted literally; doing so results in data misinterpretation. Consequently, multiple factors must be evaluated before reaching any conclusions. For insulating or low-conductivity samples, continuous electron loss during irradiation can lead to the development of a net positive surface charge. The emitted photoelectrons lose kinetic energy due to their attraction to the sample, increasing their binding energy.

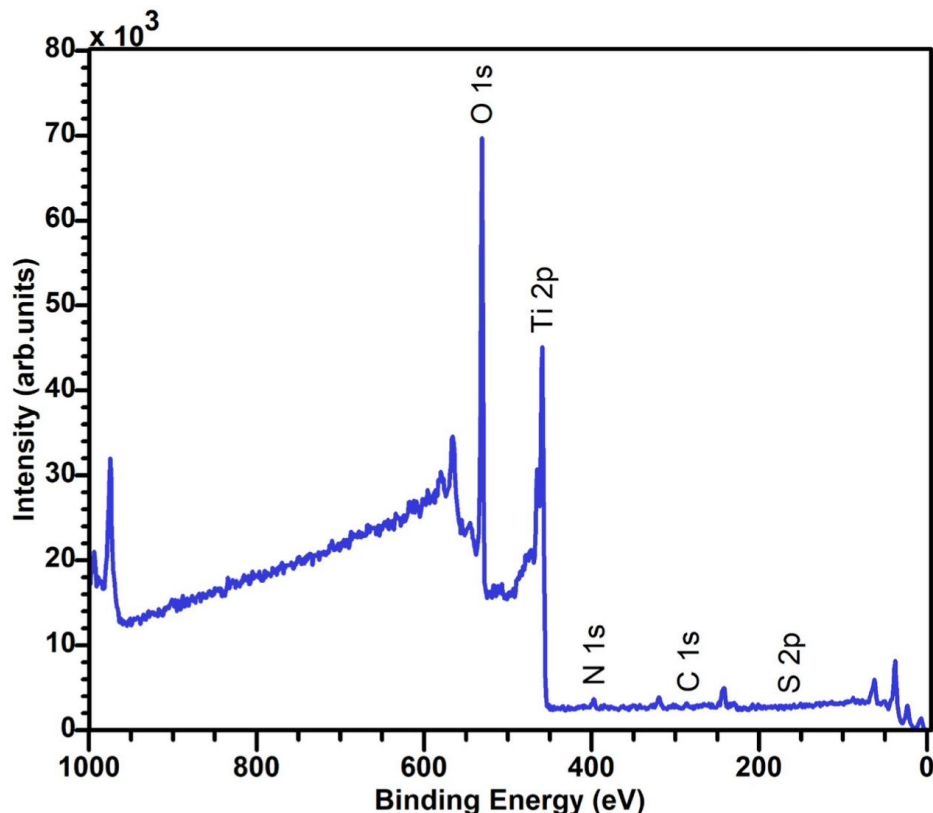


Figure 2.4: Wide XPS survey scan of the N3 molecule adsorbed on TiO_2 , demonstrating the variation of the spectrum's background in relation to binding energy. The background diminishes in steps following each peak as additional photoelectrons are removed.

The extent of the binding energy shift depends on the electrical conductivity of the sample and the effectiveness of its grounding. Therefore, the spectra must be calibrated to facilitate comparison between measurements. This can be accomplished by assigning a known binding energy value to a well-defined reference core-level peak and subsequently applying this correction to the remaining data.

The C–C environment is frequently selected and calibrated at 284.8 eV; nevertheless, the work reported in this thesis uses the O1s photoemission peak from TiO_2 . Conversely, for metallic specimens, the Fermi edge appears at 0 eV binding energy, as the binding energy scale is referenced to the Fermi level, as shown in Figure 2.4. After acquiring appropriately calibrated spectra, the background must be addressed to facilitate fitting. The background in XPS

spectra arises from inelastically scattered electrons and generally decreases as the analyser detects electrons with higher kinetic energy. At a given analyser setting, the detected signal includes both primary photoelectrons and electrons that have undergone energy loss.

When the analyser voltages are such that photoelectrons lack sufficient kinetic energy to pass through the analyser, the background decreases accordingly. This is clear from the way the background changes during a wider scan (Figure 2.4). In this work, the linear, Shirley, and Tougaard methods are employed to remove the background. The first one is the easiest because it only draws a line that goes straight from one point to another. However, the Shirley and Tougaard approaches involve more complex background modelling.

The background in XPS spectra is related to the area of the peak at higher kinetic energy [46]. At lower binding energies (corresponding to higher kinetic energies), the background intensity is governed by the observed electron flux, the inelastic mean free path of the electrons, and the relevant scattering cross-sections [47, 48]. For XPS, linear and Shirley background models are typically used, as shown in Figure 2.5. A variety of line shapes can be used to represent the spectral profile of photoelectrons accurately. Among these, the Voigt function, or more specifically, pseudo-Voigt functions, is widely used. A Voigt function consists of a convolution of Gaussian and Lorentzian components. The Gaussian component represents broadening due to instrumental effects and variations in the local chemical environment, while the Lorentzian component accounts for lifetime broadening arising from the finite lifetime of the core hole, as described by Heisenberg’s uncertainty principle.

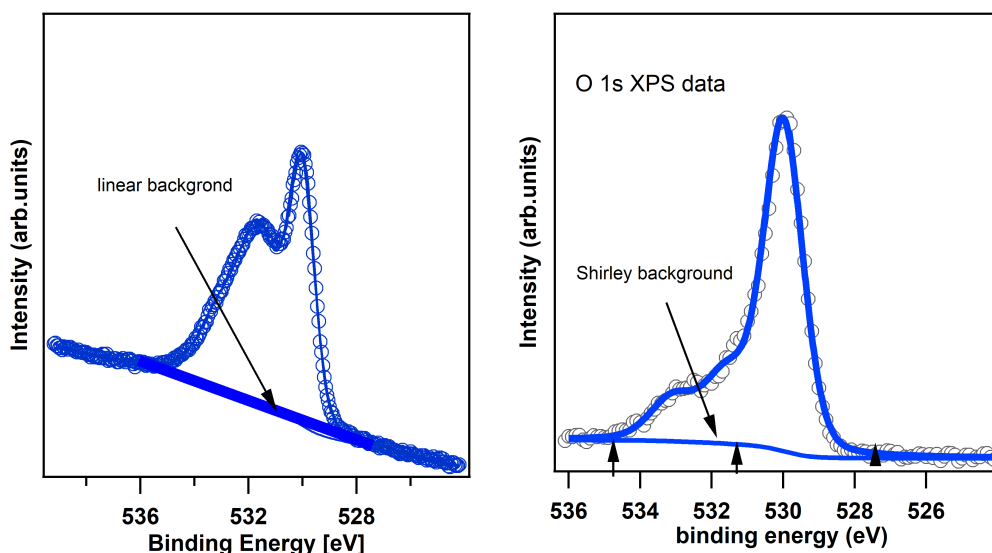


Figure 2.5: Schematic of XPS background, the left is linear and the right is Shirley background.

Because adding Voigt functions can be computationally demanding, they are often approximated by pseudo-Voigt functions. A pseudo-Voigt function is constructed as a weighted linear combination of Gaussian and Lorentzian peak shapes rather than a full convolution. As a result, a fitting parameter is introduced to control the relative contributions of the two components. This parameter, known as the Gaussian-to-Lorentzian (GL) ratio, defines the shape of the spectral line.

Most of the time, metals exhibit higher GL ratios (i.e., a more Lorentzian line shape) than molecules or compounds [49]. For a given core-level region, the GL ratio is typically kept constant across all fitted peaks, as it reflects the intrinsic physical broadening mechanisms. Therefore, the ratio should not be varied without a clear physical justification, such as a significant change in chemical environment.

2.1.3 Interpretation

Depth-Profiling

The strength of X-ray photoelectron spectroscopy (XPS) lies in the fact that relatively minor modifications to the experimental geometry or data analysis can provide additional insight into the near-surface region of a material. One such modification is angle-resolved XPS (ARXPS), in which the surface sensitivity of the measurement is enhanced by varying the angle between the analyser and the surface normal of the sample. As illustrated in Fig 2.6, tilting the sample with respect to the detector changes the electron emission geometry from normal to grazing emission.

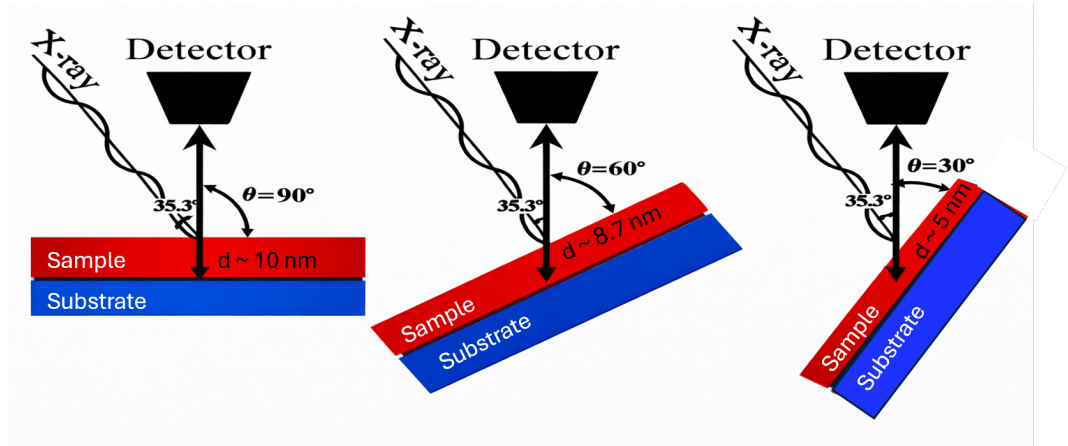


Figure 2.6: Schematic illustration of the principle of angle-resolved XPS (ARXPS). The figure is original and adapted conceptually from [50].

At grazing emission angles, the effective sampling depth is reduced because the detected photoelectrons must travel a longer path within the material before escaping the surface. Although the inelastic mean free path (IMFP) of the photoelectrons remains constant, only electrons originating from shallower depths are able to reach the analyser within its acceptance angle. Consequently, photoelectrons generated deeper within the material are increasingly attenuated. As shown in Fig 2.6, decreasing the emission angle from 90° to 30° reduces the effective sampling depth from approximately 10 nm to about 5 nm. In lay-

ered systems, such as oxidised or coated materials, the relative contributions of surface and bulk signals therefore vary with emission angle, enabling non-destructive depth profiling. In addition, ARXPS can be employed to estimate the thickness of thin overlayers, provided that the layer is sufficiently thin for photoelectrons from the underlying substrate to be detected. This thickness determination is governed by the inelastic mean free path of the photoelectrons and can be described by the Beer–Lambert law:

$$\frac{I}{I_0} = \exp\left(-\frac{d}{\lambda}\right) \quad (2.5)$$

where I is the measured intensity of a core level originating from the underlying layer, I_0 is the corresponding intensity in the absence of the overlayer, d is the thickness of the overlayer, and λ is the inelastic mean free path (IMFP). By measuring the attenuation of the substrate signal and assuming a known IMFP, the thickness of the surface layer can be quantitatively determined.

Features of XPS

Several characteristics are commonly observed during XPS. At specific core levels, the presence of multiple peaks does not necessarily indicate different chemical environments. Instead, these peaks may arise from spin–orbit coupling, where interaction between the electron’s spin and orbital angular momentum splits a single core level into two components. There are two scenarios: one in which spin and angular momentum are aligned, and another in which they are not. This is indicated by the total angular momentum quantum number, j .

$$j = l + s \quad (2.6)$$

where s represents the spin quantum number and l indicates the orbital angular momentum quantum number. The electron can be either spin-up or spin-down, allowing j to assume two values: one for the aligned state and the other for the anti-aligned state. Due to the energy associated with both

scenarios, the energy level splits, leading to photoelectrons with two distinct energies. The ratio and division of these levels are clearly defined; the former is dictated by electron degeneracy ($g = 2j + 1$), while the energy separation depends on the spin-orbit coupling strength. Spin-orbit coupling, when relevant, is going to appear in the majority of XPS spectra. Nonetheless, some characteristics are less common, many of which are referred to as ‘satellites’. Shake-up satellites represent a specific type that occurs in the spectrum presented in subsequent chapters. In this case, as the photoelectrons exit the sample, they excite higher-energy electrons into unoccupied states. As an example, this may involve electrons in the valence band being elevated to the conduction band, or electrons in the highest occupied molecular orbitals being promoted to the lowest unoccupied molecular orbitals.

Consequently, unusual peaks that lack a relationship to any chemical environment could arise at lower kinetic energy than the principal structure. Plasmon excitations are a distinct category of satellites frequently observed in the spectra of metals. In the present case, energy decays similarly to shake-up excitations; however, plasmons inside the conducting electron distribution are excited instead.

As a result, additional peaks appear at reduced kinetic energy. In some cases, these features may be neglected during spectral fitting, particularly if they lie outside the region of interest; however, they can become significant when performing background subtraction. Moreover, for certain transition metals, conventional peak fitting is often impractical due to the complexity of the spectral composition. In such cases, analysis of the satellite structure is commonly employed to distinguish between different chemical environments.

2.2 X-ray Absorption Spectroscopy

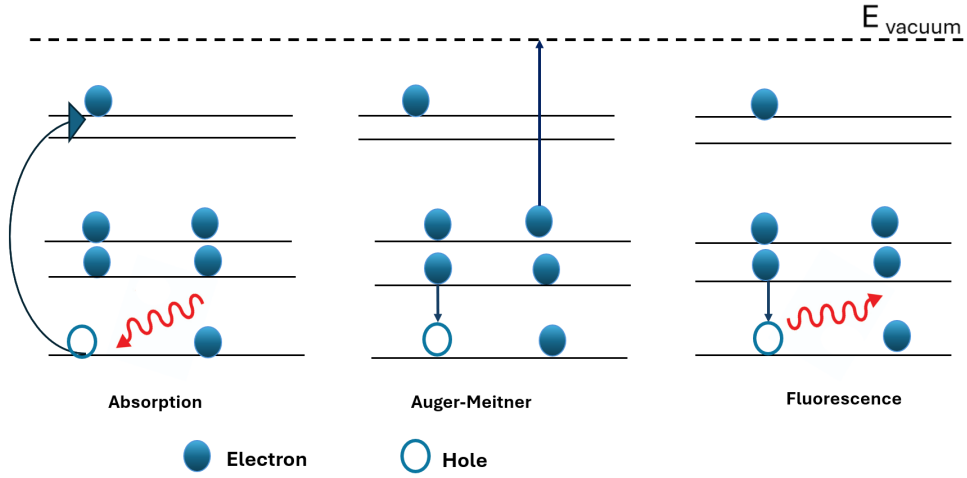


Figure 2.7: the diagram illustrates the processes involved in X-ray absorption spectroscopy (XAS). A photon is absorbed, and the resulting relaxation products, either an Auger electron or photon emission, are monitored.

2.2.1 Technique

X-ray absorption spectroscopy (XAS) is a fundamental technique in core-level spectroscopy that can function in either a photon-in, photon-out mode or a photon-in, electron-out mode. It may be referred to by alternative names, such as near-edge absorption fine structure (NEXAFS), while the underlying physics remains the same and is illustrated schematically in Figure 2.7. A photon is absorbed by the sample when its energy corresponds to the difference between the ground state and an unoccupied state, commonly referred to as a resonance. This event is linked to the different decay channels through the detection of their corresponding products, resulting in the absorption at a specific photon energy. Given the known energy of the photon, XAS offers a method for mapping the unoccupied states of the sample within the energy domain. Various methods exist to quantify absorption during X-ray absorption

spectroscopy (XAS). The most fundamental method is to measure the current of the sample during irradiation.

This operates on the principle that absorption of X-ray photons leads to the emission of photoelectrons and secondary electrons from the sample. The loss of these electrons results in a positive charge, which is compensated by an electron flow from ground, giving rise to a measurable current, commonly referred to as the ‘total electron yield’. Absorption events are associated with an increase in current through the sample (and ultimately the UHV manipulator); nevertheless, due to the often low size of the current, noise and errors may present challenges. An alternative approach involves measuring the released Auger-Meitner electrons via the hemispherical analyser in what is referred to as ‘Auger-Meitner yield’. The analyser inherently disregards contributions from alternative processes, such as further decay if the core-hole is profound. Consequently, By monitoring the yield of Auger electrons while systematically varying the incident photon energy, an X-ray absorption spectrum can be obtained, an absorption spectrum is acquired. Regrettably, this process is somewhat sluggish, as the spectra must be recorded for an extended duration to mitigate noise, with any dead time associated with the analyser and beamline optics. The most commonly recommended option is to utilise a microchannel plate (MCP) detector.

The incoming electron enters the MCP via one of the channels and collides with the inside wall, generating secondary electrons. These then generate additional electrons upon hitting the channel walls, so amplifying the signal well beyond the anticipated level for the first electron. Undesired electrons can be removed from the spectrum by introducing a reducing voltage that must be applied before entering the MCP. The N $1s$ edge occurs at around 400 eV, indicating that photons at this energy will generate N $1s$ Auger electrons while photoionising any core levels with binding energies below 400 eV. Consequently, providing a voltage of 300 V may remove a significant fraction of

the photoelectrons. The Augers-Meitner, nonetheless, have sufficient energy to enter the MCP for detection, and the resultant spectrum is described as being recorded in ‘partial electron yield’. Moreover, surface sensitivity is enhanced since only electrons that have experienced elastic scattering possess sufficient kinetic energy to reach the detector. The use of fluorescence to monitor X-ray absorption is much more bulk sensitive and so was not used for the work discussed in this thesis illustrated in Figure 2.7, is of lesser significance to our thesis and may exhibit more sensitivity to the bulk.

2.2.2 Processing & Interpretation

It can sometimes be challenging to attribute specific chemical or electrical information to an XAS spectrum without the use of computational calculations. Nevertheless, it provides insight into the positioning of the unoccupied states throughout the energy spectrum. Initially, the absorption be normalised to the flux of the incident radiation. Since the photon energy must vary incrementally, X-ray absorption spectroscopy (XAS) is commonly performed using synchrotron radiation due to the requirement for tunable photon energy. MAX IV and Diamond are modern facilities that employ continuous top-up injections for a few minutes. This maintains the intensity nearly constant. Nonetheless, normalisation is still required to correct the slight variations and potential shifts that occur during the injection. This indicates that the measured absorption correspondingly diminishes and can be adjusted by normalising to the X-ray flow. The beam’s flux is frequently monitored on a gold mesh before the sample stage. Secondly, due to an error in photon energy with each movement of the monochromator, calibration of the photon energy may be necessary. The second-order reflections of entering X-rays can be utilised, as the energy differential between features stimulated by first-order and second-order light precisely determines the photon energy.

2.2.3 Density of States Plots

XPS examines the occupied electronic states of a sample, whereas XAS probes unoccupied states created in the presence of a core hole. Using both techniques helps create a density of states (DoS) plot for a specific sample. This approach is described in reference [51]. To combine the insights from these two techniques, the unoccupied and occupied parts of the density of states are aligned on the same binding energy axis by deducting the binding energy of the relevant core level from the photon energy scale of the X-ray absorption spectroscopy. The XAS spectrum corresponds to an excited-state process involving a core hole, with the transition energy determined by the incident photon energy.

This can instead be expressed in relation to the Fermi energy by

$$h\nu = E_{\text{XAS}} - E_i \quad (2.7a)$$

$$h\nu = E_{\text{XAS}} - (E_F - E_B) \quad (2.7b)$$

$$E_{\text{XAS}} - E_F = h\nu - E_B \quad (2.7c)$$

where E_{XAS} denotes the energy in the XAS spectrum, E_i represents the ground state energy, E_F signifies the Fermi energy, and E_B indicates the binding energy of the excited core level. The equations mentioned above correspond only to the sample in a defined core-excited state and should not be taken as representative of the density of states for other excitations.

2.3 X-ray Sources

This study utilises two sources of X-rays: those produced by a laboratory source and those accessible at synchrotron facilities. The device produces X-rays by accelerating electrons from a heated filament towards a metallic target. Upon impact, the electrons lose kinetic energy, which is emitted as X-

rays. Two types of radiation are produced: characteristic and Bremsstrahlung radiation. The latter occurs as the electron is decelerated by the metal atoms, losing energy by emitting a spectrum of X-ray energies. Characteristic X-rays are generated when electrons from the filament transfer energy to bound electrons in the metal during collisions, elevating them to higher energy states or ejecting them from the metal, as needed. The core hole is then filled by a higher-energy electron after a short time, emitting an X-ray in a process known as fluorescence, shown in Figures 2.2 and 2.7. The energy of the emitted X-rays is determined by the energy difference between the initial and final electronic states and is therefore characteristic of the anode material. Examples include aluminium, silver, tungsten, and copper. A further characteristic of X-rays is the presence of several discrete photon energies. This arises from multiple allowed electronic transitions between different core and valence levels. These are constrained as

$$\Delta S = 0 \tag{2.9a}$$

$$\Delta L = 0, \pm 1 \tag{2.9b}$$

$$\Delta J = 0, \pm 1 \tag{2.9c}$$

Where ΔS , ΔL , and ΔJ represent the changes in spin, orbital angular momentum, and total angular momentum, respectively, consequently, only specific transitions are allowed. These are indicated using the Siegbahn notation, which labels characteristic X-ray lines according to the involved atomic shells. This study uses Al $K\alpha$ for laboratory-source experiments. This corresponds to the filling of an aluminium $1s$ core hole by an electron from the $2p$ orbital (specifically, $1s_{1/2} \rightarrow 2p_{3/2}$). The discrete (line-like) nature of characteristic X-ray emission from laboratory sources prevents continuous tuning of the photon energy. As a result, such sources are not suitable for X-ray Absorption Spectroscopy (XAS) and resonant spectroscopies, which require fine energy

tunability.

Synchrotrons produce X-rays using a fundamentally distinct process. A linear accelerator accelerates electrons, which are then injected into a storage ring, where their trajectories are regulated by bending magnets. As the electrons are continuously deflected, they undergo centripetal acceleration and emit synchrotron radiation, allowing precise tuning of the photon energy required for X-ray Absorption Spectroscopy (XAS) and resonant spectroscopies.

By precisely controlling the beam's direction, maintaining low pressures to reduce scattering, and applying intermittent minor accelerations to compensate for energy loss, the longevity of the electrons within the ring is extended, rendering the designation 'storage ring' fitting. Beamlines are strategically placed at specific points around the ring to collect the radiation produced as electrons pass through the ring. These are linear assemblies comprising multiple optical stages that concentrate and select the required energy of the X-rays. At the end of the beamline is the experimental end station, where spectra are acquired. X-rays are generated when the electron changes its trajectory at the bending magnet. Nevertheless, it was immediately recognised that this radiation was not the optimal solution, as it is emitted in a horizontal scattering, resulting in incomplete utilisation of the emitted radiation at the end station [52]. Consequently, insertion devices are prevalent in synchrotrons today. These generate highly intense X-rays and consist of two well-known, qualitatively identical types: wigglers and undulators. This work exclusively uses undulators, which are composed of a series of magnetic poles that disturb the beam, causing it to oscillate as it traverses its route. The outcome is a coherent X-ray beam exhibiting a continuous energy distribution, wherein the brilliance of the source is proportional to the square of the number of oscillations, N^2 [52]. Synchrotron radiation produces a continuous spectrum of X-rays. In contrast, the spectrum from a laboratory source is distinct. In both

cases, monochromators are used to select a narrow bandwidth of X-ray photon energies rather than simply eliminating unwanted radiation. For hard X-rays, this selection is achieved through Bragg diffraction from crystal planes, where the photon energy is tuned by rotating the crystal according to Bragg's law $n\lambda = 2d \sin \theta$. Consequently, the wavelengths are diffracted variably, enabling the selection of energy through the rotation of the crystal.

This aspect is particularly advantageous for synchrotrons, as it enables the selection of photon energy as needed. Soft X-rays present further challenges, as suitable crystals may be adversely affected by thermal load or degradation [53]; hence, plane gratings are frequently utilised as an alternative. In this work, TiO_2 nanoparticles (NPs) were studied using the FlexPES beamline at the MAX-IV Laboratory in Sweden. In addition, N₂ adsorption on $\text{TiO}_2(110)$ was examined by normal incidence X-ray standing wave (NIXSW) measurements using the I09 beamline at Diamond Light Source Laboratory, United Kingdom.

2.4 Resonant Photoelectron Spectroscopies

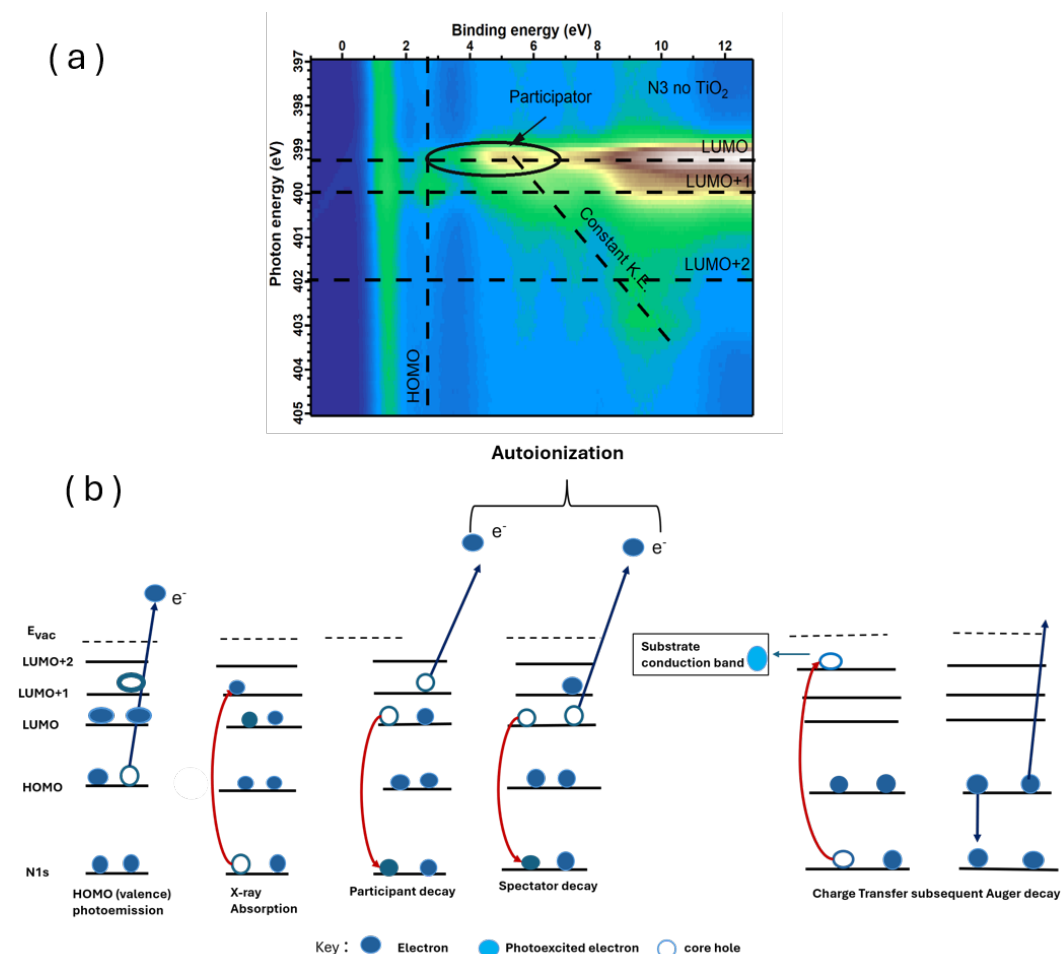


Figure 2.8: (a) RPES map, obtained at the FLEXPES beamline of the Max IV Laboratory, showing a thick coverage of N3 dye molecules no TiO₂. This system illustrates the electron charge transfer between the surface and the molecules. Essential characteristics are outlined. Photoemission HOMO characteristics observed at the LUMO resonance have been enhanced due to participator decay channels (circled). Dashed lines indicate characteristics of continuous kinetic energy. (b) Schematic representation of the operational principle of resonant photoemission spectroscopy (RPES) adapted from [54]. The RPES map and electron transition diagram were developed based on my experimental data. The presentation style follows the approach outlined in previous work [25].

Resonant Photoelectron Spectroscopies

Resonant photoelectron spectroscopy (RPES) is a powerful tool to help understand charge delocalisation and charge transfer mechanisms in organic photo-

voltaics and dye-sensitised solar cells (DSSCs). RPES combines XPS measurements with XAS. In this process, an electron moves from the core hole to an unoccupied bound state. The kinetic energy of the photoelectrons, and consequently the binding energy, is determined during a subsequent Auger-Meitner decay at varying photon energies. This method allows for the examination of the decay mechanism at an adsorbate-surface interface. The RPES data is often displayed as two-dimensional graphs. In these graphs, the intensity of released valence photoelectrons is shown as a function of both incident photon energy and their measured binding energy. Figure 2.8 illustrates an RPES map obtained for a thick coverage of N3 molecules, on TiO_2 . This map displays several noticeable features that indicate electron transfer between the surface and the molecule.

This example involves measuring the photoelectron spectrum of the valence band area, within a constant binding energy window, as a function of photon energy across the N 1s absorption edge. The horizontal dashed lines indicate intensity related to excitation into the lowest unoccupied molecular orbital (LUMO) states, which appear at a constant excitation energy. Constant kinetic energy characteristics, shown by diagonal dashed lines in the monolayer RPES spectrum, exhibit linear dispersion across the RPES binding energy range as photon energy increases. The diagonal features are primarily associated with the Auger-Meitner decay channel, while the spectator features are expected to show minimal dispersion. The photon energy resolution was sufficiently high compared to the resonance width, ensuring that the spectator features do not disperse significantly. The HOMO states are enhanced when they are in resonance with the LUMO, as indicated by the vertical dotted lines. This behaviour arises from the participator decay channel, where the excited electron is first promoted to the LUMO state.

It then returns to fill the core hole, and the energy from this transition is given to an electron in a HOMO state, ejecting it into the vacuum. The final state after participator decay matches that of conventional HOMO photoemission. The two processes are indistinguishable in observed binding energy. However, their existence is indicated by an increase in HOMO intensity when measured at the LUMO excitation energy.

Core-hole Clock Spectroscopy

RPES can provide insight into the charge transfer dynamics of dye-semiconductor systems with great precision through the core-hole clock approach [55]. This occurs due to the core holes generated as the molecule is excited to an unoccupied state. Resonant photoelectron spectroscopy relies on the formation of a core-excited state in which the photo-excited electron remains localised on the dye molecule. Under these conditions, resonant decay channels give rise to additional spectral features. If the excited electron is instead rapidly injected into the TiO_2 substrate, the resonant condition is lost, and the core hole decays predominantly via conventional Auger or fluorescence pathways. Changes in the resonant spectral features provide insight into the competition between electron localisation and ultrafast charge transfer in dye-sensitised systems. Consequently, in the context of DSSCs, if charge injection into TiO_2 occurs rapidly compared to the core-hole lifetime, few resonant characteristics are detected. The periods for charge transfer are associated with intensity using

$$\tau_{CT} = \tau_{CH} \cdot \frac{\frac{I(\text{mono}_{\text{RPES}})}{I(\text{mono}_{\text{NEXAFS}})}}{\frac{I(\text{multi}_{\text{RPES}})}{I(\text{multi}_{\text{NEXAFS}})} - \frac{I(\text{mono}_{\text{RPES}})}{I(\text{mono}_{\text{NEXAFS}})}} \quad (2.8)$$

Here, “mono” refers to measurements performed on a dye monolayer adsorbed on the TiO_2 surface, whereas “multi” denotes measurements acquired from multilayer dye films on TiO_2 . τ_{CT} denotes the charge transfer time and τ_{CH} represents the core-hole lifetime, while I_{RPES} and I_{XAS} indicate the intensity of the unoccupied state in question measured during RPES and XAS, respec-

tively, with τ_{CH} determining the accuracy of the computed transfer times. This often occurs on the order of femtoseconds, and the methodologies depend on the precision with which the intensities can be measured.

Consequently, it has been estimated that charge transfer time can be measured to an order of magnitude both above and below τ_{CH} [55]. At this juncture, it is crucial to elucidate the methodology for calculating charge transfer time from an RPES spectrum. A map of valence spectra is constructed from data obtained at changing photon energies. The resonant energies are found, and the appropriate region is integrated to generate an absorption spectrum similar to XAS. The intensity of the participant is assessed and compared to a similar XAS spectrum, which indicates the state's sensitivity to RPES in relation to XAS. The ratios are input into Equation (2.8) to compute charge transfer times.

2.5 Sample preparation techniques

2.5.1 Electrospray Deposition

Many molecules are too sensitive to undergo thermal deposition, necessitating alternative preparation techniques. Electrospray deposition provides a gentle method for depositing large and fragile molecules (such as N3 in Chapter 4 and D5 in Chapter 5) without degradation. Figure 2.9 illustrates the configuration of a vacuum electrospray deposition system, in which ionised molecular species are transferred from the emitter through a sequence of differentially pumped stages into the ultra-high vacuum (UHV) chamber. The system comprises an emitter and entrance capillary followed by a series of skimmer cones that progressively reduce the pressure, enabling the transport of molecular ions into UHV for deposition onto the sample.

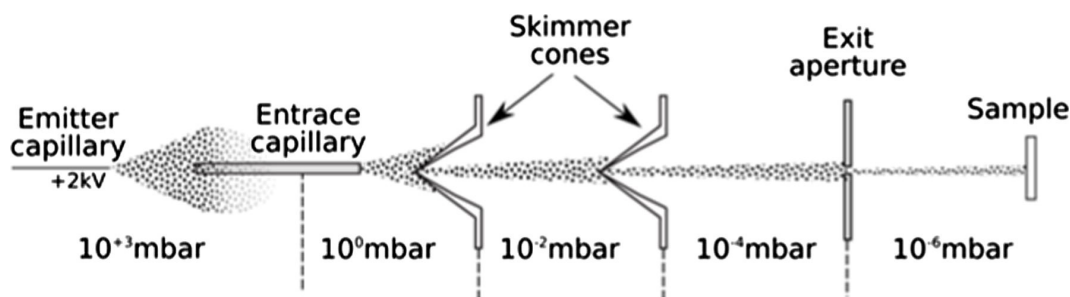


Figure 2.9: Diagram illustrating the electrospray deposition principle, in which a jet of ionised molecular solution travels through chambers that are differentially pumped until it reaches ultra-high vacuum (UHV). Adapted from Ref [56].

Electrospray deposition was performed using the setup shown in Figure 2.10. A modified configuration including an ion gate was employed for selected experiments; details of the ion-gate operation and its effect on deposition are described in Section 4.2.1.

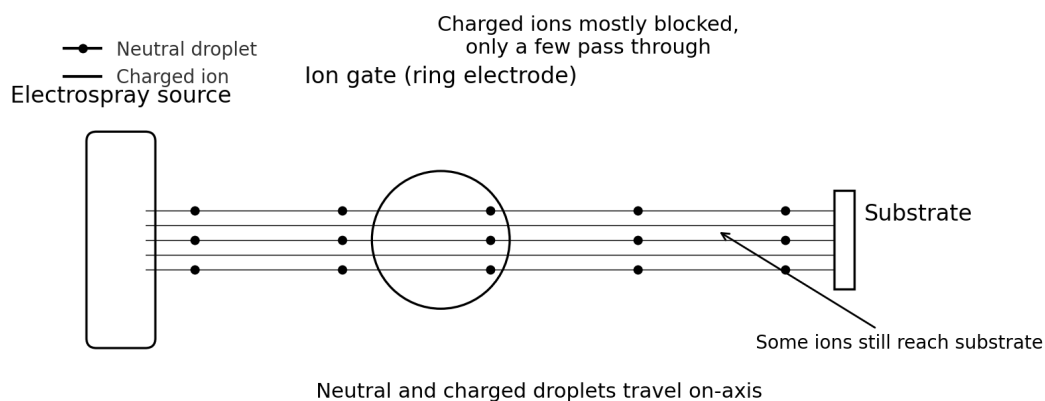


Figure 2.10: Schematic illustration of the electrospray deposition (ESD) setup with the ion gate. Neutral droplets containing dye molecules travel along the beam axis and reach the substrate. The ion gate, implemented as a ring electrode, repels most charged ions, though a small fraction can still pass through due to their high kinetic energy.

The ion gate was added to the electrospray deposition setup to test whether it could filter out the ionic component of the molecular beam, allowing only neutral D5 molecules to reach the substrate. By blocking solvent-derived ions and other charged species, the ion gate aimed to make films mainly from neutral D5. This method allows for more controlled, representative adsorption

on the TiO_2 surface.

A stainless steel emitter with an internal diameter of $100\ \mu\text{m}$ (New Objective, USA) was used to deliver a concentrated D5 solution at a rate of $0.3\ \text{ml hr}^{-1}$. The emitter was biased at 2.3 kV relative to ground to ionise the solvent and generate a stable electrospray jet. The resulting plume entered an aperture with an internal diameter of 0.5 mm to promote solvent evaporation, before passing through a series of differentially pumped stages with progressively larger apertures. The base pressure of the UHV chamber was typically 1×10^{-9} mbar, increasing to 10^{-8} mbar when the gate valve was open without applied voltage, and to the low-mid 10^{-7} mbar range when both the valve and voltage were engaged, indicating that D5 constituted the majority of the spray.

2.5.2 Drop-casting deposition

Drop-casting is widely used to apply thin films to solid surfaces, especially in laboratories. First, a solution or dispersion is prepared by mixing the target material, such as polymers, nanoparticles, or dyes, with a volatile solvent. A small droplet of this solution is deposited on a substrate. When the solvent evaporates, either at room temperature or under conditions like heating or reduced pressure, a thin residue remains. Solution concentration, droplet size, evaporation rate, and substrate wettability affect the film's thickness and uniformity.

Drop casting is a simple process that requires minimal equipment, but provides limited control over film morphology and thickness uniformity. However, it often fails to produce uniform films over large areas. The film thickness can vary with changes in surface tension and evaporation, resulting in thinner edges and a thicker centre. Despite these issues, drop casting is valuable for preliminary testing, material evaluation, and proof-of-concept work in areas such as sensor development, electronics, and photovoltaic devices [57]. In

this work, samples with thin, medium, and thick coverage of N3 dye on TiO_2 nanoparticles were prepared using the drop casting method.

2.5.3 Dye sensitisation of TiO_2 surfaces

TiO_2 NPs-dye sensitizer

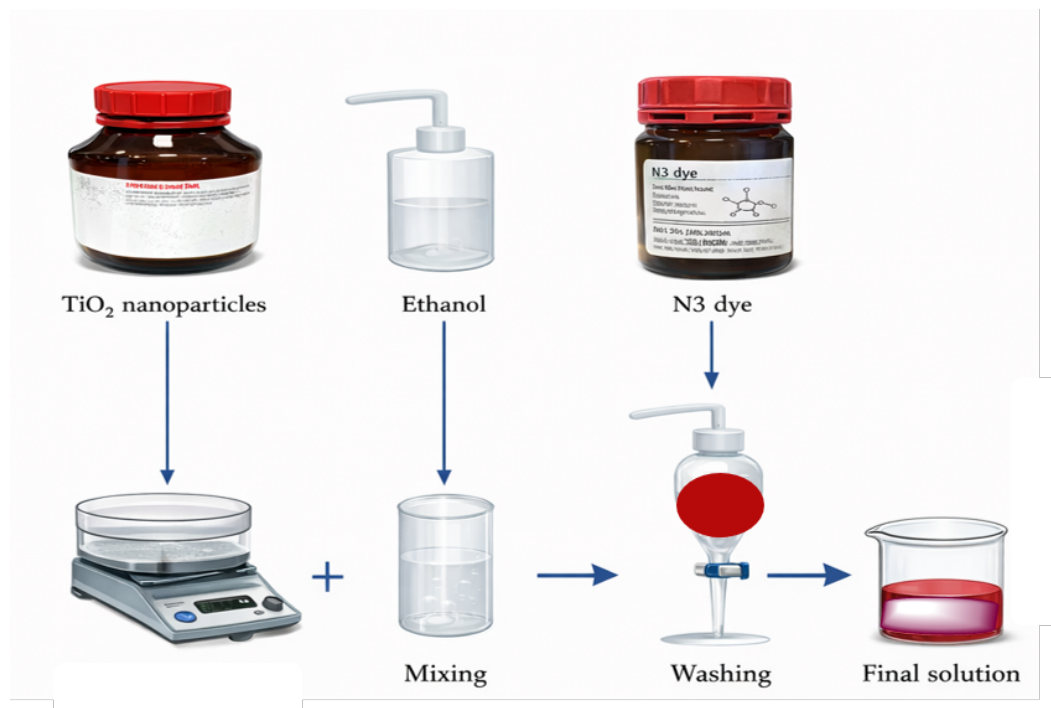


Figure 2.11: Schematic illustration of the preparation of an N3-TiO₂ nanoparticle sensitizer. TiO₂ nanoparticles are dispersed in ethanol and sensitised with N3 dye, followed by washing to remove unbound dye. The resulting suspension is subsequently used for electrospray deposition. Figure created by the author.

In this method, we prepared N3-dye-sensitized TiO₂ nanoparticles by first mixing TiO₂ NPs with ethanol, subsequently adding a small amount of N3 as shown in Figure 2.11. We kept the solution sitting for a day to allow N3 to dissolve in the solvent and bond to TiO₂ NPs. Afterwards, we repeatedly washed the solution to remove excess, loosely attached dye. This process causes TiO₂ NPs to settle in the container, leaving only chemisorbed dye molecules, while the physisorbed ones are washed away. This washing step was repeated multiple times to ensure complete removal of weakly bound (physisorbed) dye

molecules, leaving only the strongly chemisorbed N3 dye molecules that form covalent bonds with the TiO_2 surface through their carboxylate groups.

Dye-sensitized mesoporous TiO_2

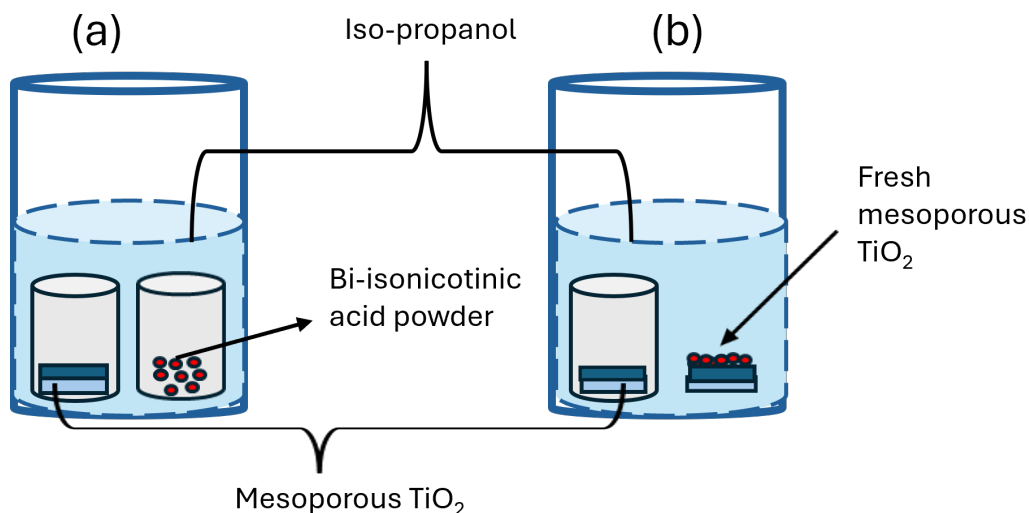


Figure 2.12: Schematic illustration of the ex-situ synthesis of a bi-isonicotinic acid monolayer on mesoporous TiO_2 . Grey cylinders represent schematic sample containers used during the immersion process.

The monolayer was prepared by immersing the samples in a saturated molecular solution in a suitable solvent until formation of a surface layer, as illustrated in Figure 2.12. The samples were subsequently washed and soaked in fresh solvent for several hours, and the soaking–washing cycle was repeated until the solution became clear. Care was taken to ensure that no residual solvent remained on the surface to avoid disruption or contamination of the monolayer. Because bi-isonicotinic acid is only sparingly soluble in isopropanol, extended adsorption was carried out under controlled conditions. The mesoporous TiO_2 substrates were left in the solution for over one week, with periodic solvent replacement to remove excess physisorbed molecules. The procedure followed the method reported in Ref [25].

2.6 The X-ray Standing Wave Method

2.6.1 Miller index

The Miller index (hkl) is a standard method for describing crystallographic planes within a solid. The parameters are determined by the points where the plane intersects the x-, y-, and z-axes: a, b, and c. The Miller index is calculated as $(hkl) = (1/a, 1/b, 1/c)$, then simplified to the smallest set of integers. In our study, we examined rutile TiO_2 and deposited the N3 dye on the substrate along the rutile $\text{TiO}_2(110)$ direction. We selected the plane (220), which is parallel to (110), as shown in Figure 2.13. This plane is crucial for understanding where the Ru atom and C 1s in COOH and thiocynate are located in 3D space (x, y, z).

The Miller indices (110) and (220), shown in Figure 2.13 (right panel), define the crystallographic planes of the rutile $\text{TiO}_2(110)$ substrate used in the NIXSW analysis. The adsorption geometry of N3 on $\text{TiO}_2(110)$ is inferred from the XSW measurements rather than from the Miller indices themselves. The (220) planes are parallel to the (110) surface. In the NIXSW geometry, the surface normal defines the plane orientation, and under normal-incidence conditions, the incident X-ray beam is aligned parallel to the surface normal. The reflected beam, therefore, propagates along the same direction, forming the standing-wave field normal to the surface. The interplanar spacing, d_{hkl} , corresponds to the distance between crystal lattice planes, as defined in Equation (2.10). Specifically, it D_{110} is 3.2 Å and D_{220} 1.6 Å, with lattice constants $a = 4.593$ Å and $c = 2.959$ Å for rutile TiO_2 (tetragonal). The left panel illustrates the (101) and (110) planes at a polar angle of 67°, where red arrows indicate the incident beam, green arrows represent the reflected beam, and blue arrows denote the direction of the XSW, which is normal to the Bragg planes. In X-ray standing-wave (XSW) experiments, selecting the Miller in-

dices is crucial, as the chosen (hkl) plane defines the Bragg reflection and thus the resulting standing-wave field within the crystal. When the Bragg condition is satisfied for a specific plane, the standing-wave nodes and antinodes are positioned relative to that crystallographic plane. Consequently, selecting any reflection shifts the position of the standing-wave field within the lattice, thereby directly affecting the sensitivity of the measurements to atom positions or adsorbed molecular groups at the surface.

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{l^2}{c^2} \quad (2.10)$$

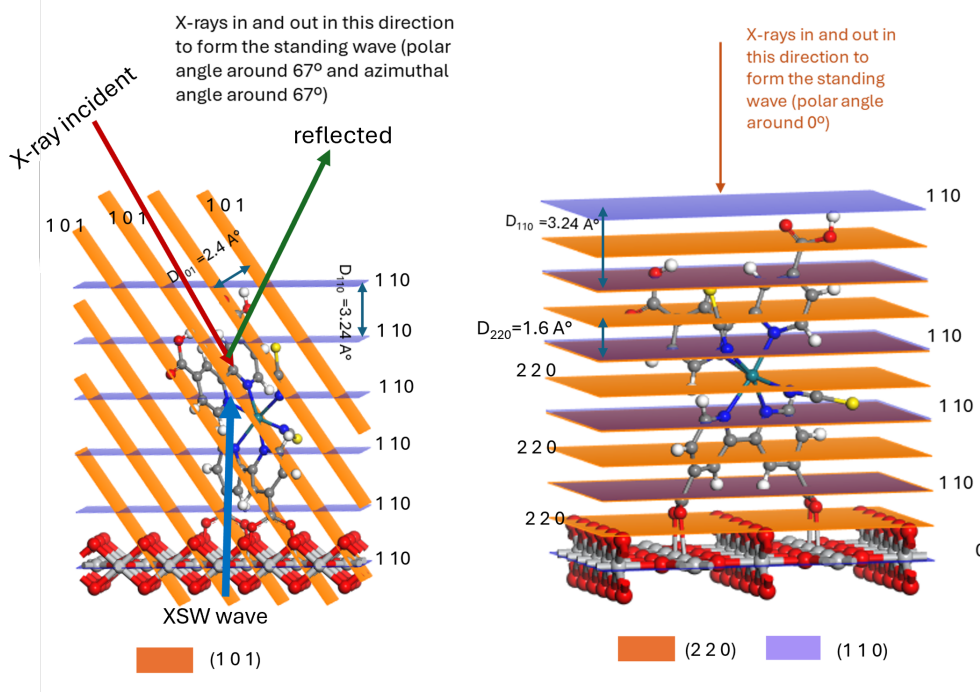


Figure 2.13: Formation of X-ray standing waves from specific Bragg reflections of rutile $\text{TiO}_2(110)$. The left panel illustrates the standing-wave field generated from the (101) and (110) planes, while the right panel shows the NIXSW geometry based on the (220) and (110) planes. Red arrows indicate the incident X-ray beam, and green arrows represent the reflected beam. The indicated angles correspond to the Bragg angle θ relative to the crystallographic planes and are shown schematically for clarity (not to scale). In the normal-incidence geometry (right panel), the incident beam is aligned parallel to the surface normal, and the standing-wave field is formed along the direction normal to the substrate surface.

2.6.2 Normal Incidence X-ray Standing Wave (NIXSW) analysis

Principles and Description

X-ray standing-wave (XSW) analysis uses Bragg reflection, in which a crystal lattice coherently scatters incident X-rays. This produces a standing-wave field near and above the substrate surface, enabling precise determination of atomic positions. This standing wave, in turn, enables precise determination of the positions of surface atoms. The normal incidence X-ray standing wave (NIXSW) technique limits X-ray incidence to the normal direction of the (hkl) planes. NIXSW applies to a wide range of single-crystal samples. This technique is suitable for nearly all single-crystal samples, as most metal crystals exhibit numerous surface and bulk imperfections at non-normal angles of incidence. These imperfections prevent the effective use of other incidence angles. Therefore, normal incidence is typically required. XSW requires long-range order across single-crystal surfaces to establish a coherent standing wave successfully. Each element present on the substrate surface can be analysed independently. By using primary and secondary emission peak data, such as X-ray photoelectrons and Auger-Meitner electrons, chemical information can be obtained.

The XSW technique provides two structural parameters per (hkl) set of planes: the coherent position (P_c) and the coherent fraction (F_c) per element. These parameters are related to the spatial distribution of atoms with respect to the (hkl) scatterer planes. To further determine atom positions in three dimensions, at least two sets of planes are required: one parallel to the sample surface and one or more at an angle to it. With multiple planes, this approach enables triangulation of atomic positions. Indeed, triangulation is a principal strength of XSW. However, the method is limited by the finite number of available (hkl) planes.

This can limit the possible coherent position and fraction pairs. This scenario can prevent the determination of complete atomic arrangements. In the next section, we will discuss the Miller index and its importance in the triangulation plane.

2.6.3 XSW theory

Bragg's Law

NIXSW Description

Two coherent waves, possessing a defined wavelength and phase relationship, overlap to generate standing waves. Bragg's law states that

$$n\lambda = 2d_{hkl} \sin \theta_B \quad (2.10)$$

In this context, n represents the order of diffraction and must be an integer for constructive interference. d_{hkl} denotes the spacing between the scattering planes, and θ_B is the Bragg angle between the incident X-ray beam and the crystal planes.

Under NIXSW conditions, the standing wave field is oriented normal to the crystal surface. Figure 2.14 illustrates Bragg diffraction and X-ray standing wave (XSW) formation on rutile TiO_2 . The incident X-ray beam impinges upon the (110) planes at the Bragg angle, resulting in a reflected beam at the same angle. The interference between the incident and reflected waves generates a standing wave field normal to the crystal planes.

The adsorption geometry of dye molecules can be determined by comparing the nodes and anti-nodes of the standing wave field under different Bragg conditions.

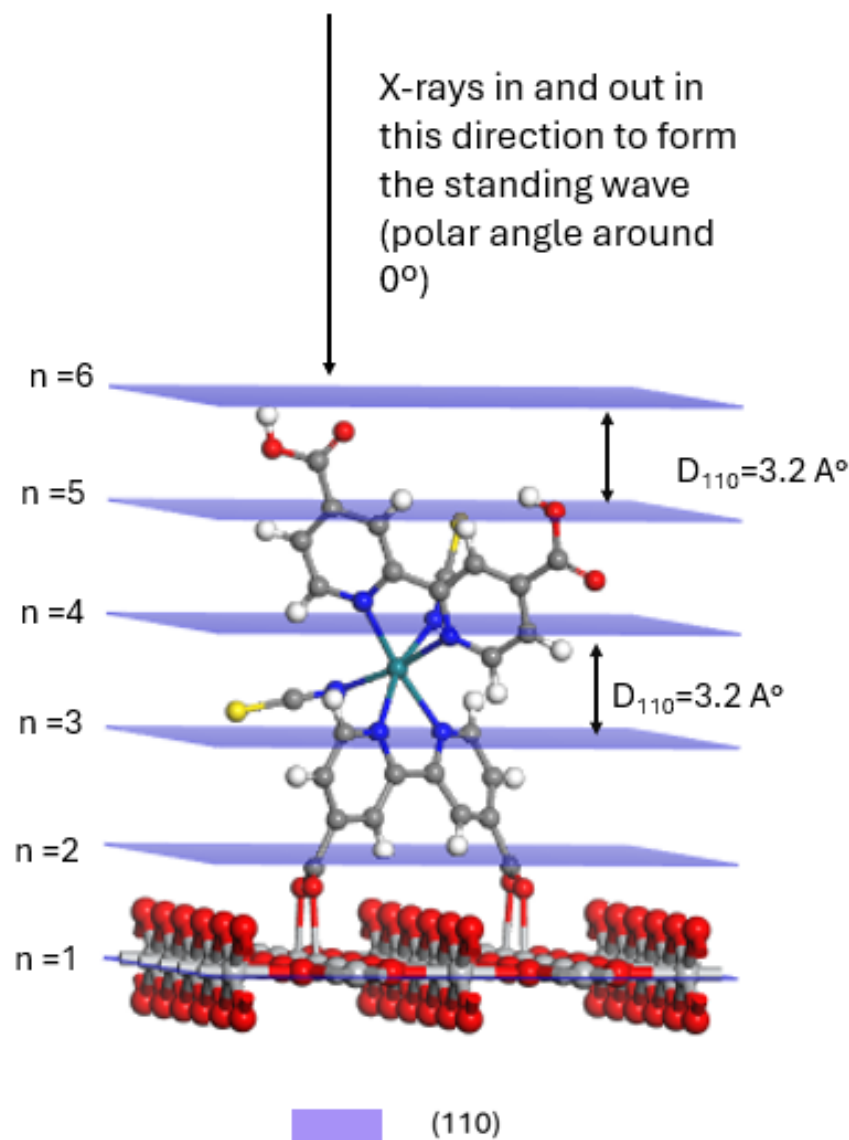


Figure 2.14: Schematic illustration of Bragg diffraction and X-ray standing wave (XSW) formation for the TiO_2 (110) planes. The incident and reflected X-ray beams interfere constructively at the Bragg angle, generating a standing wave field normal to the crystal planes.

2.7 Supporting Techniques

2.7.1 Density Functional Theory (DFT)

In this thesis, Chapter 4 was dedicated to the study of D5, where DFT calculations were carried out by the author to investigate its electronic structure

using the Gaussian 09 software package. Geometry optimisations were performed at the B3LYP/6-31G(d) level to obtain stable configurations prior to further analysis. Time-dependent DFT (TD-DFT) was subsequently applied to analyse the electronic behaviour of D5, including the calculation of absorption spectra and excited-state properties. The polarisable continuum model (PCM) was employed to represent the acetonitrile environment. These calculations were conducted to support the experimental results by providing insight into the electronic structure and charge-transfer processes within the D5 system. Similar computational approaches have previously been reported by Sen and Grob [58], and the methodology adopted here follows those established studies while applying the calculations directly within the present work.

In Chapter 5, additional DFT calculations were performed by the author to investigate the optimisation and geometry of N3 on rutile $\text{TiO}_2(110)$. These calculations were used to support the XSW study by determining the atomic positions relative to the $\text{TiO}_2(110)$ surface and comparing them with the experimentally obtained coherent positions. Figure 5.7 presents the calculated structure of N3 on rutile $\text{TiO}_2(110)$ after geometry optimisation using the Dmol3 software, following previously reported implementations [59, 60].

Matlab software

David Duncan has written two main MATLAB scripts for XSW data analysis. The initial script generates XSW data to calculate plane triangulation. The second script is essential, as it provides results demonstrating the key parameters in the calculations: the coherent position (P_c) and the coherent fraction (F_c). These findings inform the comprehensive discourse in Chapter 5.

Chapter 3

Charge Transfer and Adsorption of N3 Dye on TiO₂: Single Crystal, Mesoporous, and Nanoparticles

3.1 Introduction

One of the most researched dyes for dye-sensitised solar cells (DSSCs) is N3 (cis-bis(isothiocyanate)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium (II)) [61]. For DSSC applications, a thin layer of N3 dye molecules adsorbed onto the surface of rutile titanium dioxide exhibits visible-light sensitivity [62]. N3 dye has been previously studied on surfaces made of rutile titanium oxide [24], anatase [29], mesoporous TiO_2 [25], aluminium oxides [26, 31, 63, 64]. The chemical structure of N3 dye is shown in Figure 3.1. The adsorption behaviour and binding geometries of the N3 dye on TiO_2 surfaces have been discussed in detail in Chapter 1. Here, only a summary is provided, where N3 is known to bind to rutile $\text{TiO}_2(110)$ through deprotonated carboxylic groups forming bidentate configurations, as reported in previous studies [24, 65, 66]. It has been reported that it binds to rutile $\text{TiO}_2(110)$ through the deprotonation of two carboxylic acid groups of its bi-isoinc acid ligands, giving a 2M-bidentate connection [24, 25, 29, 65–68].

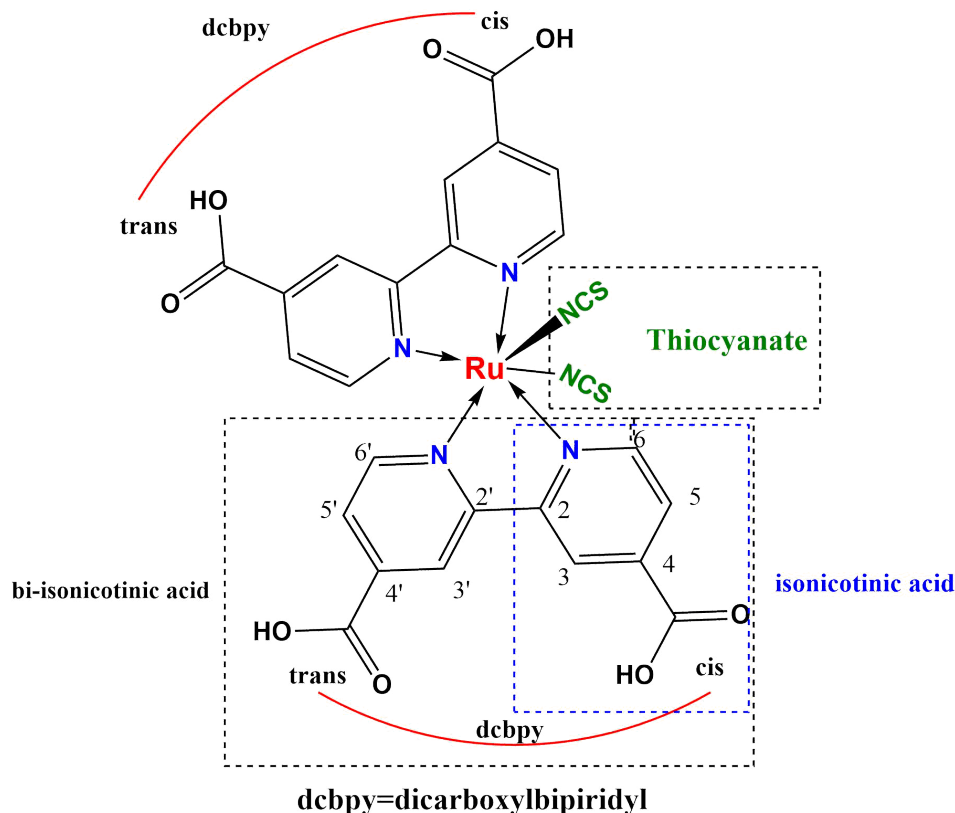


Figure 3.1: The chemical structure of the N3 dye (cis-bis(isothiocyanato)bis(2,2-bipyridyl-4,4-dicarboxylato)-ruthenium (II) (N3). The molecule is a metal-organic complex with a ruthenium centre, two thiocyanate ligands, and two bi-isonicotinic acids.

3.2 The evolution of N3 film thickness on single-crystal rutile $\text{TiO}_2(110)$

3.2.1 Experimental Methods

The preparation and deposition were carried out in our lab at the University of Nottingham. The first stage was cleaning the $\text{TiO}_2(110)$ substrate multiple times by sputtering with 2 kV Ar^+ ions for 20 mins, followed by annealing at 600°C. The rutile $\text{TiO}_2(110)$ substrate was ready to deposit the N3 solution on it, as shown in the Figure 3.2. The N3 solution was prepared in advance: a small amount of N3 dye was dissolved in ethanol as described in section 2.5.1. A laser was used to pre-align the molecular spray deposition system. The laser beam was guided through the electrospray entrance capillary to trace the

3.2. THE EVOLUTION OF N3 FILM THICKNESS ON SINGLE-CRYSTAL RUTILE $\text{TiO}_2(110)$

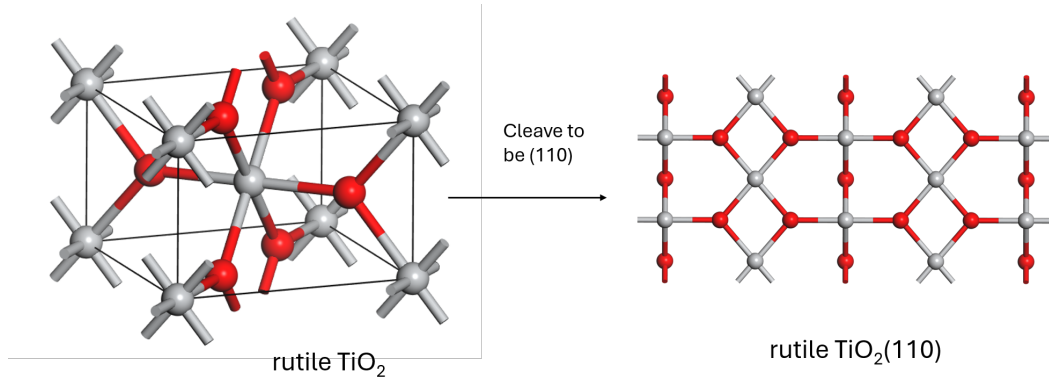


Figure 3.2: The left panel shows rutile TiO_2 after cleavage; the resulting surface corresponds to single-crystal rutile $\text{TiO}_2(110)$. Grey spheres represent Ti atoms, and red spheres represent O atoms.

molecular beam path and define the deposition spot inside the XPS chamber, enabling accurate substrate positioning prior to N3 deposition. The first spray lasted 5 minutes, followed by a wide scan to assess surface coverage. This process was repeated for 40 minutes to obtain various N3 coverages on $\text{TiO}_2(110)$. The electrospray system is physically isolated from the preparation chamber using an ultra-high vacuum (UHV) gate valve. The pressure within the preparation chamber was measured to be 10^{-10} mbar when the gate valve was closed. However, when the valve was opened and the electrospray technique was not in progress, the pressure increased to 10^{-8} mbar. The chamber pressure saw an increase to 10^{-7} mbar during the electrospray process.

This additional pressure can be attributed to solvent molecules that have not been entirely removed from the molecular beam. Based on the time range, the deposition coverage will change. In this chapter, the coverage is modified by varying the deposition time to 5, 10, 20, and 40 minutes. Subsequently, measurements are taken at each deposition time. The XPS binding energy scale was calibrated by referencing the Ti $2p_{3/2}$ substrate peak, fixed at 458.8 eV [69].

The Shirley and linear backgrounds were removed from the spectra. A linear background was selected because it provides a stable approximation of the in-

elastic background in this energy range without introducing overfitting, unlike higher-order polynomial functions. “Following background subtraction, the spectra were fitted using a pseudo-Voigt function, defined as a weighted combination of Gaussian and Lorentzian components. The dataset was modelled using 30% Lorentzian and 70% Gaussian contributions to approximate a Voigt lineshape as discussed in section 2.1.2 in chapter 2.

3.2.2 Results and Discussion

The photoemission spectra arise from sub-monolayer, few-layer, and multilayer coverages of N3 on TiO₂. The photoemission spectra of the samples’ surface coverage are classified as sub-monolayer, few layers, or multilayer. Monolayers consist of adsorbed molecules directly on the surface. In multilayer films, the molecules in the upper layer are too far from the substrate to interact with it. By utilising XPS to create a comprehensive picture of the molecular-surface bonding process, this chapter will also provide maps illustrating the sample’s intensity versus time variations.

Figure 3.3 shows the O 1s XPS spectra acquired at different deposition times to illustrate a wide range of surface coverages. The monolayer is defined here as the coverage at which the molecular XPS signal reaches saturation and the substrate O 1s attenuation becomes constant; accordingly, 5 min corresponds to sub-monolayer coverage, while 10 min is assigned as approximately one monolayer. The spectra for these coverages exhibit similar components and are therefore considered near-monolayer. Four components were required to fit the 5–10 min samples, whereas the 20 and 40 min samples exhibit multilayer behaviour and were fitted using three components. The main peak at 530 eV corresponds to TiO₂. For coverages deposited for 5–10 minutes, the peak at 531.4 eV is attributed to C=O, which undergoes deprotonation to form COO[−]. Adsorption of aromatic carboxylic acid molecules on TiO₂ promotes proton removal and the formation of a 2M-bidentate bridging mode, in which the two oxygen atoms become chemically equivalent upon adsorption. Addi-

tional components at 532 eV and 531.3 eV are assigned to C=O and H–O–Ti species, respectively. The Ti–OH peak partially overlaps with adjacent components; however, its position was fixed at the reported value of 531.3 eV and constrained using consistent line-shape parameters, ensuring a physically meaningful separation rather than overfitting, in agreement with [70].

The bisonicotinic acid forms different bonding motifs with the TiO₂ substrate: a 2M bidentate bridging bond and a monodentate H-bridging bond [71]. This study extends previous reports by providing a time-dependent XPS analysis of the O 1s components, allowing the evolution from sub-monolayer to multilayer coverage to be resolved and clarifying the relative contributions of C=O, COO[−], and Ti–OH species during adsorption. The carboxyl groups in the N3 molecule contain equal numbers of C=O and C–OH functionalities. Each oxygen atom shares an electron with the TiO₂ substrate to form a bond. If the N3 molecule is attached to the TiO₂ base, the ratio will be 2:1:1:1 to COO[−]:C=O:H–O–Ti:C–OH. In this study, at 5 and 10 minutes, the ratio of oxygen in a molecule COO[−]:C=O:H–O–Ti:C–OH is 2:1:1:0. This result is consistent with the monolayer behaviour reported previously [24]. During the 5- and 10-minute deposition times, the C–OH peak was absent because the signal was too weak to detect C–OH, as the recent study [72] found. For deposition times of 20 and 40 minutes, there are two small peaks: carbonyl (C=O) at 531.4 eV and hydroxyl (C–OH) at 532.9 eV. These ratios likely approach 1:1, as multilayer species do not undergo the same deprotonation behaviour observed at approximately monolayer coverage.

Following 20 and 40 minutes of deposition, ratios of C=O to C–OH are 4:3 and 4:4, respectively. Hence, after 20 minutes of deposition, the measured signal is influenced by both the top unbonded layer, which shows a 1:1 ratio, and the underlying monolayer that lacks OH groups. The signal reflects how

3.2. THE EVOLUTION OF N3 FILM THICKNESS ON SINGLE-CRYSTAL RUTILE $\text{TiO}_2(110)$

these two layers interact, producing ratios between 0 and 1 that indicate the combined effect of the distinct bonding configurations in each layer.

3.2. THE EVOLUTION OF N3 FILM THICKNESS ON SINGLE-CRYSTAL RUTILE $\text{TiO}_2(110)$

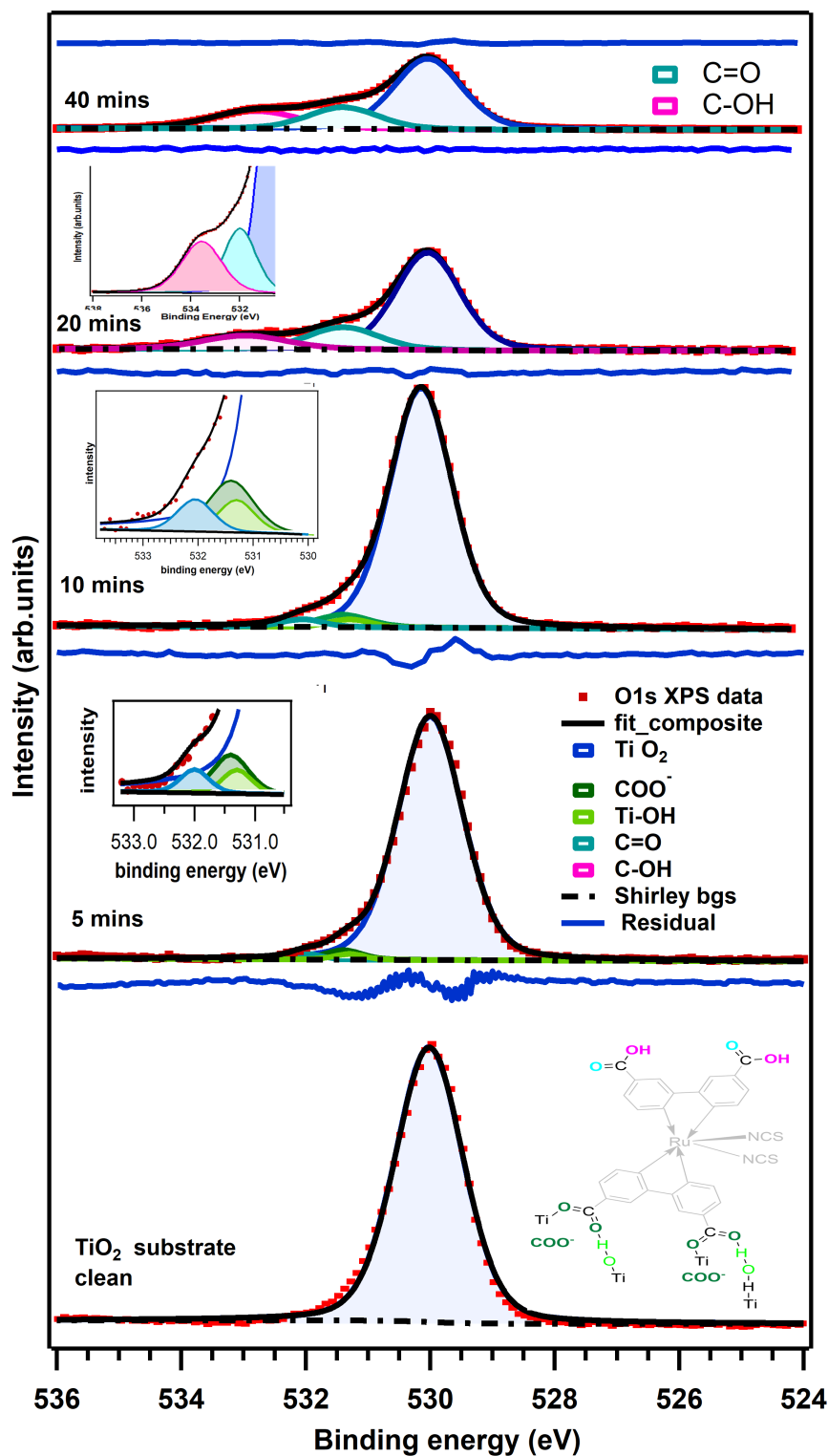


Figure 3.3: O 1s photoemission spectra of N3 adsorbed on rutile $\text{TiO}_2(110)$ at various deposition times. A Shirley background was subtracted from the spectra prior to fitting; 'bgs' denotes the Shirley background subtracted. The residual spectra are displayed above each main spectrum.

The XPS measurement of the S 2*p* spectra for 5 mins, 10 mins, 20 mins, and 40 mins of deposition is represented in Figure 3.4, S 2*p* is a doublet state with a spin-orbit coupling of 1.1 eV [73, 74]. In the N3 molecule, two thiocyanate ligands (NCS) contain two S atoms. In this study, the deposition times of 5, 10, and 20, 40 minutes are similar. There is one S atom at low binding energy (161.8 eV) with an intensity ratio of 2:1 where the intensity increases as the time of deposition increases; this agrees with a previous study [24], which found two different chemical environments of sulphur atoms for the monolayer: one of S bonded to the surface and another stuck out of the vacuum. This study shows one S, indicating that within 5,10 minutes after deposition, TiO₂ bonds to TiO₂, and at 20 minutes, it could be bonded or not bonded to the TiO₂. However, at 40 minutes of deposition, the S is non-bonded to the TiO₂ surface because the sample has a thick coverage, so the result expected for the S atom won't interact with the surface. In this case, disagree with the findings of a previous study at the multilayer coverage [24].

The XPS measurements of the S 2*p* spectra acquired at deposition times of 5, 10, 20, and 40 minutes are shown in Figure 3.4. The overall S 2*p* intensity increases with deposition time, reflecting increased surface coverage, while the relative intensity of the spin-orbit split components remains constant at the expected 2:1 ratio. The doublet separation is ~1.2 eV, consistent with previous reports [24]. In the N3 molecule, the thiocyanate (NCS) ligands contribute two sulphur atoms, and a component at low binding energy (161.8 eV) is observed whose intensity increases with deposition time. In agreement with [24], the spectra are dominated by a single sulphur chemical environment represented by a spin-orbit doublet. The increase in overall intensity indicates higher coverage rather than the formation of additional sulphur species, while at longer deposition times the increased thickness reduces direct interaction with the TiO₂ surface, consistent with multilayer growth.

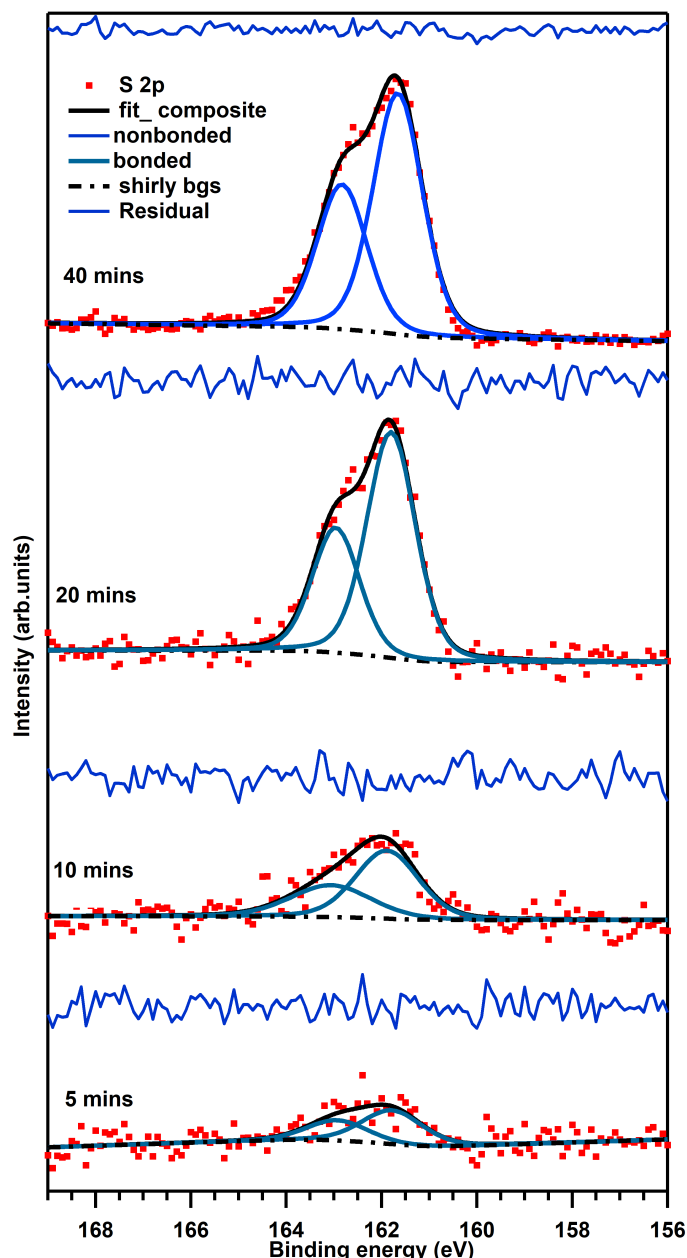


Figure 3.4: S 2*p* photoemission spectra of N3 adsorbed on rutile $\text{TiO}_2(110)$ at different deposition times. The spectra show comparable line shapes with a spin-orbit splitting of 1.2 eV and an intensity ratio of 2:1 for the $2p_{3/2}$ and $2p_{1/2}$ components. A Shirley background was subtracted from all spectra prior to fitting. The fitted components and composite fits are shown together with the residual spectrum in each case.

The C 1*s* and Ru 3*d* spectral data are shown in Figure 3.5. The spectrum was fitted using components assigned to pyridine C–C, pyridine C–N, carboxyl, and thiocyanate species, together with a Ru 3*d* doublet. The relative component ratio is 6:4:2:1, consistent with the expected stoichiometry. At 280.7 eV,

the intensity ratio between the Ru $3d_{5/2}$ and Ru $3d_{3/2}$ components is 3:2, as expected, with a spin-orbit splitting of 4.2 eV [75]. For deposition times of 5 and 10 minutes, the COO^- species formed via deprotonation on the TiO_2 surface appears at 288.6 eV and is slightly higher in binding energy than the COOH component observed at 20 minutes, indicating interaction of the carboxyl group in bi-isonicotinic acid with the TiO_2 surface.

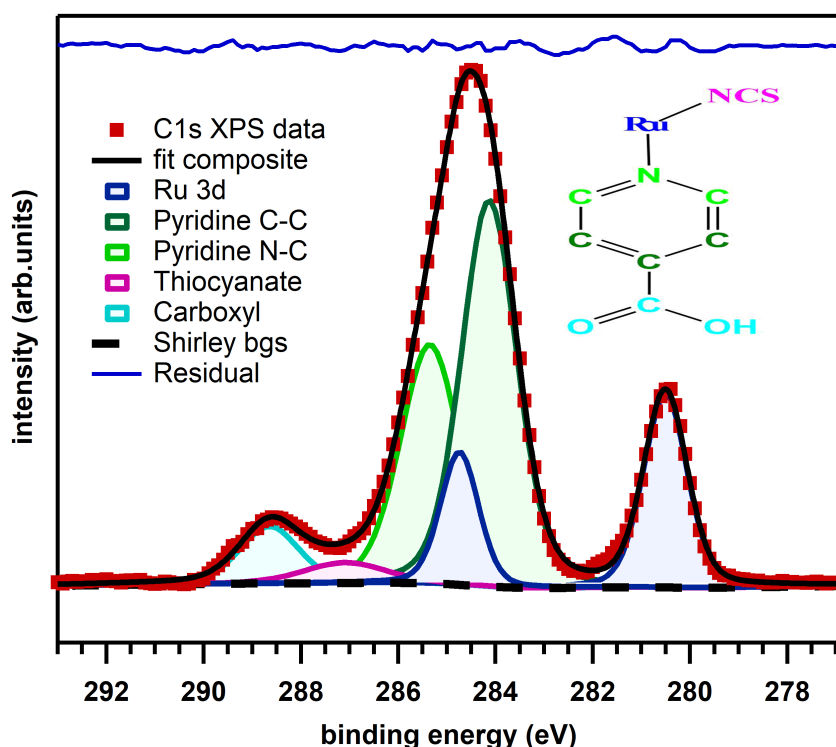


Figure 3.5: C 1s photoemission spectrum of N3 adsorbed on rutile $\text{TiO}_2(110)$. A single representative spectrum is shown, as all spectra acquired at 5, 10, 20, and 40 minutes of deposition exhibit similar line shapes. A Shirley background was subtracted prior to fitting, and the residual spectrum is displayed above the fit.

Figure 3.6 shows the N 1s photoelectron spectrum of N3 on rutile $\text{TiO}_2(110)$. It has been fitted to nitrogen in the pyridine rings (N–C) at 399.8 eV and to thiocyanate (NCS) at 397.6 eV. The ratio between them is 2:1, respectively. There is an extra peak at 396.07 eV; it corresponds to the molybdenum Mo $3p_{3/2}$ peak, indicating contamination from the sample holder. The N 1s XPS

spectrum of molecules shows that all N3 molecules interact entirely with the TiO_2 surface.

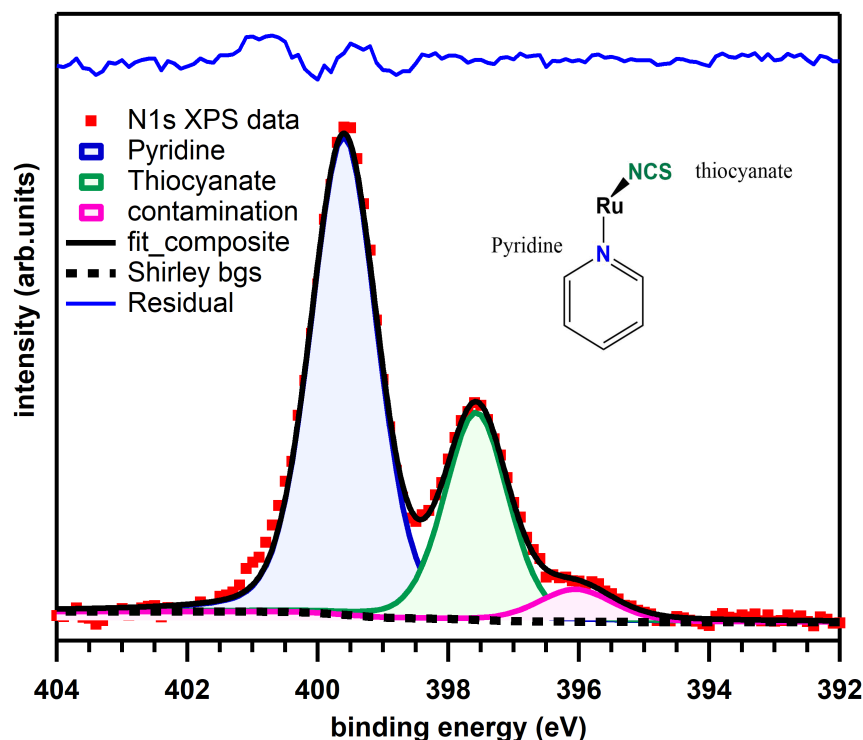


Figure 3.6: N 1s photoemission spectrum of N3 adsorbed on rutile $\text{TiO}_2(110)$. Shirley’s background information was removed from the dataset. Above the spectrum is displayed the residual spectrum.

Figure 3.7 presents the Ti 2p photoelectron spectrum of N3– $\text{TiO}_2(110)$. The spectrum shows two oxidation states for Ti: Ti^{+4} and Ti^{+3} , as well as Ru $3p_{3/2}$ at 461.1 eV. For Ti^{+4} , the Ti $2p_{3/2}$ peak appears at 458.6 eV and the Ti $2p_{1/2}$ peak at 464.4 eV. For Ti^{+3} , the Ti $2p_{3/2}$ peak is at 457.1 eV and the Ti $2p_{1/2}$ peak at 462.7 eV. These doublet states have a spin-orbit splitting of 5.7 eV [76]. The Ru $3p_{3/2}$ component appears in the fit at 461.1 eV. The corresponding Ru $3p_{1/2}$ peak is not shown in this window, as a spin-orbit splitting of 22 eV separates it [77]. These features confirm the presence of both Ti^{+4} and Ti^{+3} oxidation states.

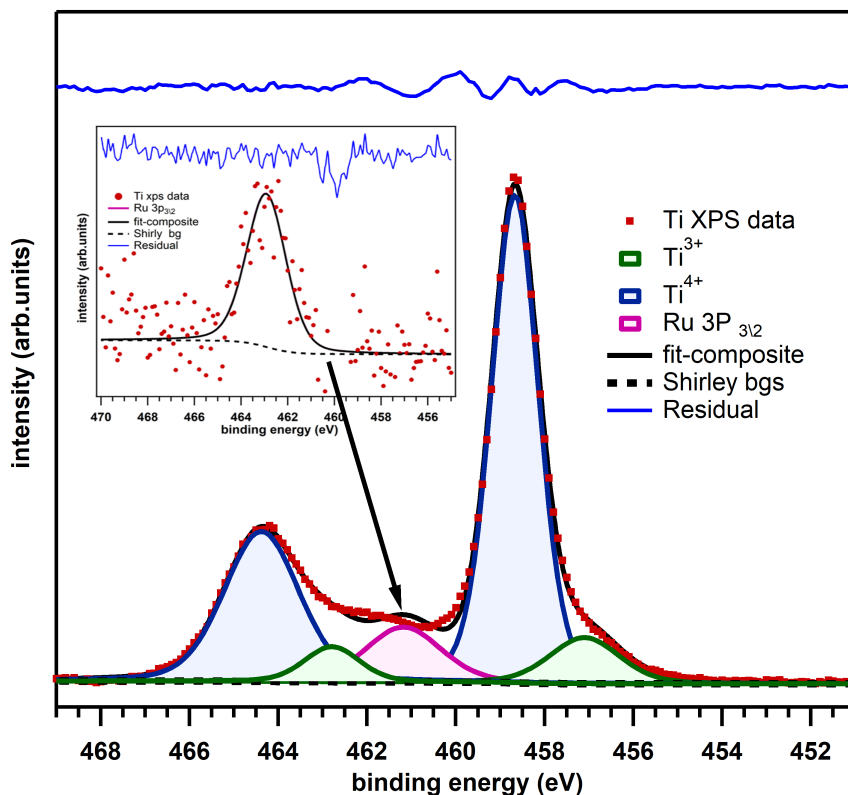


Figure 3.7: Ti 2*p* photoemission spectra of N3 adsorbed on rutile $\text{TiO}_2(110)$. A Shirley background has been subtracted. Above the spectrum is displayed the residual spectrum.

The Ru 3*p*_{3/2} feature at 461.1 eV. This signal was obtained by subtracting the fitted Ti 2*p* component from the spectrum to isolate the weak Ru contribution overlapping with the Ti 2*p* region. The presence of the Ru 3*p* peak confirms adsorption of the N3 molecule on the $\text{TiO}_2(110)$ surface.

3.2. THE EVOLUTION OF N3 FILM THICKNESS ON SINGLE-CRYSTAL RUTILE TiO₂(110)

Table 3.1: Peak BEs (eV) according to the 5 minutes, 10 minutes, 20 minutes, and 40 minutes of deposition of TiO₂(110) by in situ deposition, where all spectra are calibrated to Ti 2*p* at 458.8 eV.

PES		Peak BEs (eV)			
		5 mins	10 mins	20 mins	40 mins
O 1 <i>s</i>	TiO ₂	530.0	530.0	530.0	530.0
	COO [−]	531.4	531.4	—	—
	H—O—Ti	531.3	531.3	—	—
	C=O	532.0	532.0	531.4	531.4
	C—OH	—	—	532.9	532.9
S 2 <i>p</i>	S—nonbonded	—	—	—	161.6
	S—bonded	161.8	161.8	161.8	—
Ru 3 <i>d</i>		280.7	280.7	280.7	280.5
C 1 <i>s</i>	Pyridine C—C	284.1	284.1	284.5	284.1
	Pyridine N—C	285.7	285.7	285.3	285.6
	NCS	287.1	287.1	287.1	287.6
	COOH	288.6	288.6	288.3	288.6
N 1 <i>s</i>	NCS	397.6	397.6	397.9	397.6
	Pyridine	399.8	399.8	399.8	399.8
Ti	Ti ⁺⁴ 2 <i>p</i> _{3/2}	458.6	458.6	458.6	458.6
	Ti ⁺³ 2 <i>p</i> _{3/2}	457.1	457.1	457.1	457.1
Ru 3/2		461.1	461.1	461.1	461.1

3.2.3 Deposition and film growth of N3 on $\text{TiO}_2(110)$

O 1s XPS as a function of film thickness

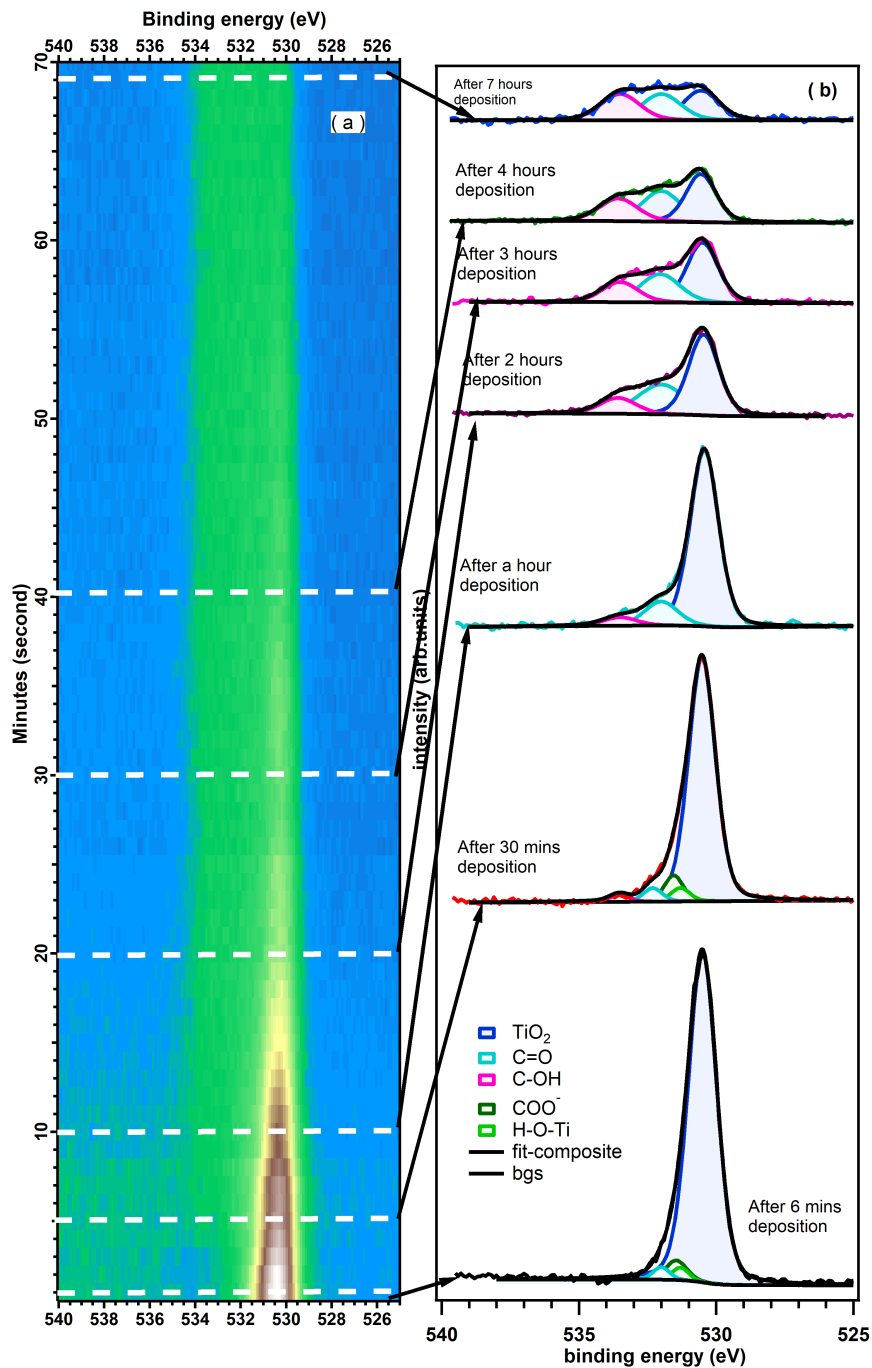


Figure 3.8: The evolution of the O 1s spectrum during N3 molecule deposition on rutile $\text{TiO}_2(110)$ is illustrated, where (a) shows the O 1s map, and (b) shows the fitted spectra with time.

The N3 molecules deposit onto the rutile $\text{TiO}_2(110)$ surface, and the film thickness increases with deposition time. The O 1s signals change, as shown in Figure 3.8. We break down the procedure into two parts: (a) A map displays the distribution of the O 1s signal. (b) Spectra are obtained from this map to demonstrate the spatial changes of the O 1s signal during deposition. These derived spectra are fitted with XPS to examine the O 1s signal components and changes (b). The map in 3.8(a) is 2D, where the x-axis represents the binding energy (eV) and the y-axis is time (minutes). It shows the high intensity at 530.5 eV, which belongs to $\text{O}_{\text{lattice}}$ in Ti.

While Figure 3.3 presents fitted O 1s spectra at selected deposition times, Figure 3.8 provides a time-resolved representation derived from the O 1s map, capturing the continuous evolution of the spectral features during deposition. The two figures are therefore complementary, with Figure 3.3 offering quantitative peak fitting and Figure 3.8 illustrating the overall temporal progression. In Figure 3.8(b) were obtained by extracting horizontal line profiles from the map at 6 and 30 minutes, and at 1, 2, 3, 4, and 7 hours of deposition. The signal is so weak that the high intensity of the peak is $\text{O}_{\text{lattice}}$ in the Ti surface. Three peaks in the molecule contribute to O. The dark green line corresponds to COO^- at 531.4 eV. The carboxyl group in N3 deprotonates when it's bonded to the Ti substrate, and the light green represents the H atom from the hydroxyl (OH) group bonded to O in the Ti substrate. It's at 531.3 eV, which agrees with this study [70].

The third peak is C=O at 532 eV, indicating that the entire molecule is bonded to the TiO_2 surface at the thinnest molecular coverage. However, the C–OH peak is missing in this spectrum because the signal is so weak and there is not much N3 compared to the time that those peaks were deposited, as shown in Table 3.2, where the ratio of COO^- :H–O–Ti: C=O: C–OH for the sample, which is after 6 minutes of deposition, is 2:1:1:0. The spectrum shows four peaks after 30 minutes of deposition. They are COO^- at 531.4 eV, H–O–Ti

3.2. THE EVOLUTION OF N3 FILM THICKNESS ON SINGLE-CRYSTAL RUTILE TiO₂(110)

at 531.3 eV, C=O at 532.3 eV, and C–OH at 533.5 eV. The ratio of intensity to these peaks is 2:1:1:0.5. Here, the relatively low C–OH intensity suggests that a fraction of the hydroxyl groups may remain non-bonded to the surface, possibly forming intramolecular hydrogen interactions rather than surface bonds.

For longer deposition times (1–7 hours), the spectra show that there are two peaks contributed by C=O and C–OH at BEs of 532 and 533.5 eV, respectively. The C=O intensity decreases by the time of deposition until to be equal to the C–OH intensity as spectrum in after seven hours deposition this means that the deposition is multilayer, which agrees with many studies [24, 31, 63], and in study at the end of this chapter Section 3.2.5.

Table 3.2: The binding energy of peak of O 1s growth deposition on TiO₂(110), the ratio refers to the relative peak intensity obtained from the fitted O 1s components COO[−]:H–O–Ti: C=O: C–OH.

Deposition time	O _{lattice}	COO [−]		H–O–Ti		C=O		C–OH	
	BE (eV)	BE (eV)	Ratio	BE (eV)	Ratio	BE (eV)	Ratio	BE (eV)	Ratio
6 mins	530.5	531.4	2	530.3	1	532.0	1.0	533.5	0.5
30 mins	530.5	531.4	2	530.3	1	532.3	1.0	533.5	0.5
1 hour	530.5					532.0	2.7	533.5	1.0
2 hours	530.5					532.0	2.4	533.5	1.0
3 hours	530.5					532.0	1.5	533.5	1.0
4 hours	530.5					532.0	1.3	533.5	1.0
7 hours	530.5					532.0	1.0	533.5	1.0

C 1s XPS as a function of film thickness

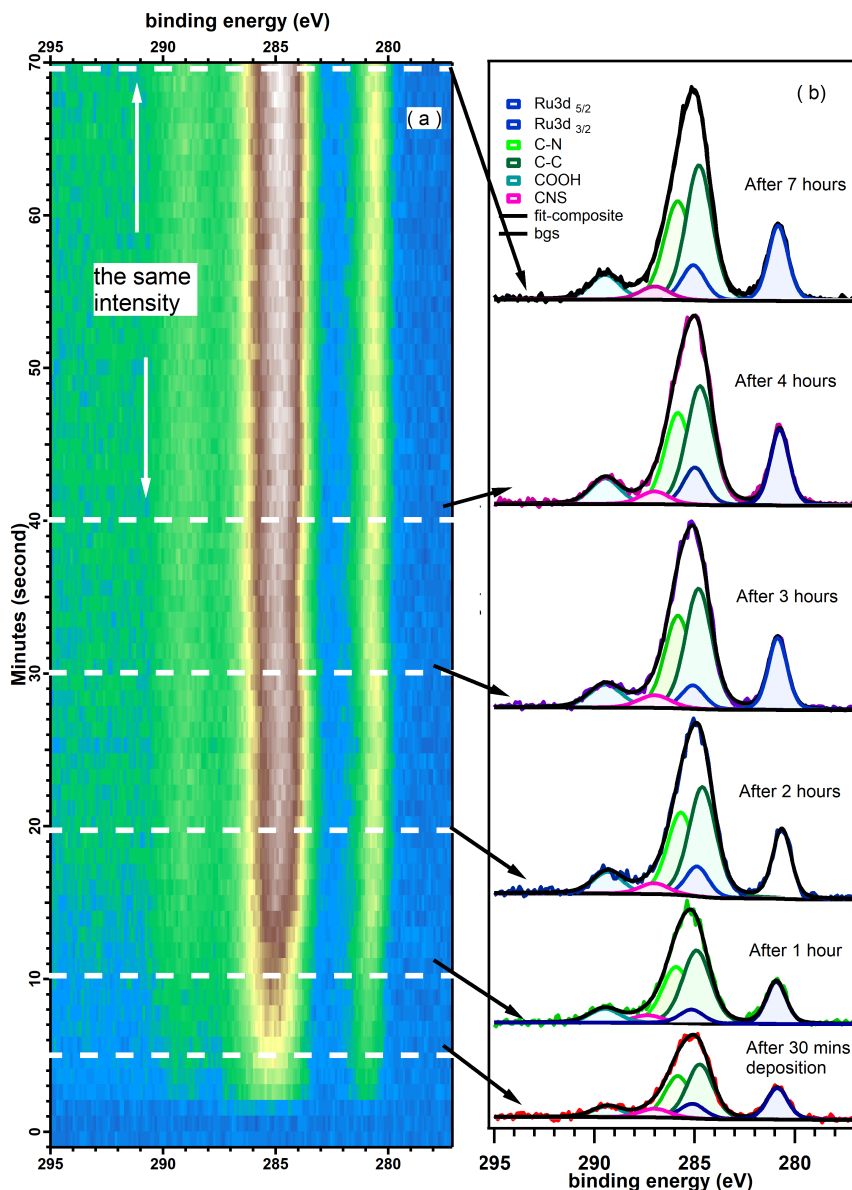


Figure 3.9: The evolution of the C 1s XPS spectrum as a function of N3 deposition time on rutile $\text{TiO}_2(110)$ is illustrated, where (a) shows the C 1s map, (b) represents the fitted spectra with time.

Figure 3.9 includes an extensive overview of the evolution of the C 1s signal over carbon deposition in two complementary formats. Figure 3.9(a) presents a two-dimensional intensity map with binding energy (eV) on the x-axis and deposition time (minutes) on the y-axis, which clearly shows the gradual enhancement of the C 1s signal centred at 285 eV during the deposition process.

Figure 3.5 provides a representative fitted C 1s spectrum illustrating the component assignments, whereas the following analysis focuses on the evolution of these components with deposition time. Figure 3.9(b) presents a series of spectra extracted from the 2D map using horizontal line profiles. The spectra show a consistent increase in C 1s signal intensity as the deposition time increases from 30 minutes to 7 hours. It presents comprehensive peak-fitted spectra for six time intervals (30 minutes, 1, 2, 3, 4, and 7 hours), illustrating the progression of chemical composition. Each spectrum was decomposed into fitted components: Ru $3d_{5/2}$ at 280.9 eV and its spin-orbit split counterpart Ru $3d_{3/2}$ at 285.1 eV (with a separation of 4.2 eV); C–C and C–N bonds (indicated by dark and light green peaks) at 284.7 eV and 285.8 eV, respectively, maintaining a consistent ratio of 3:2; CNS species (represented by a pink peak) at 287 eV; and COOH functional groups at 289 eV, with a CNS:COOH ratio of 1:2. This peak assignment and the proportional amounts of carbon species are consistent across all time points, indicating a steady chemical environment throughout the growth phase. The spectrum analysis suggests that although the total carbon content increases with deposition duration, the relative distribution of carbon bonding environments remains relatively stable, supporting a consistent growth mechanism during deposition.

Ti 2p spectrum as a function of film thickness

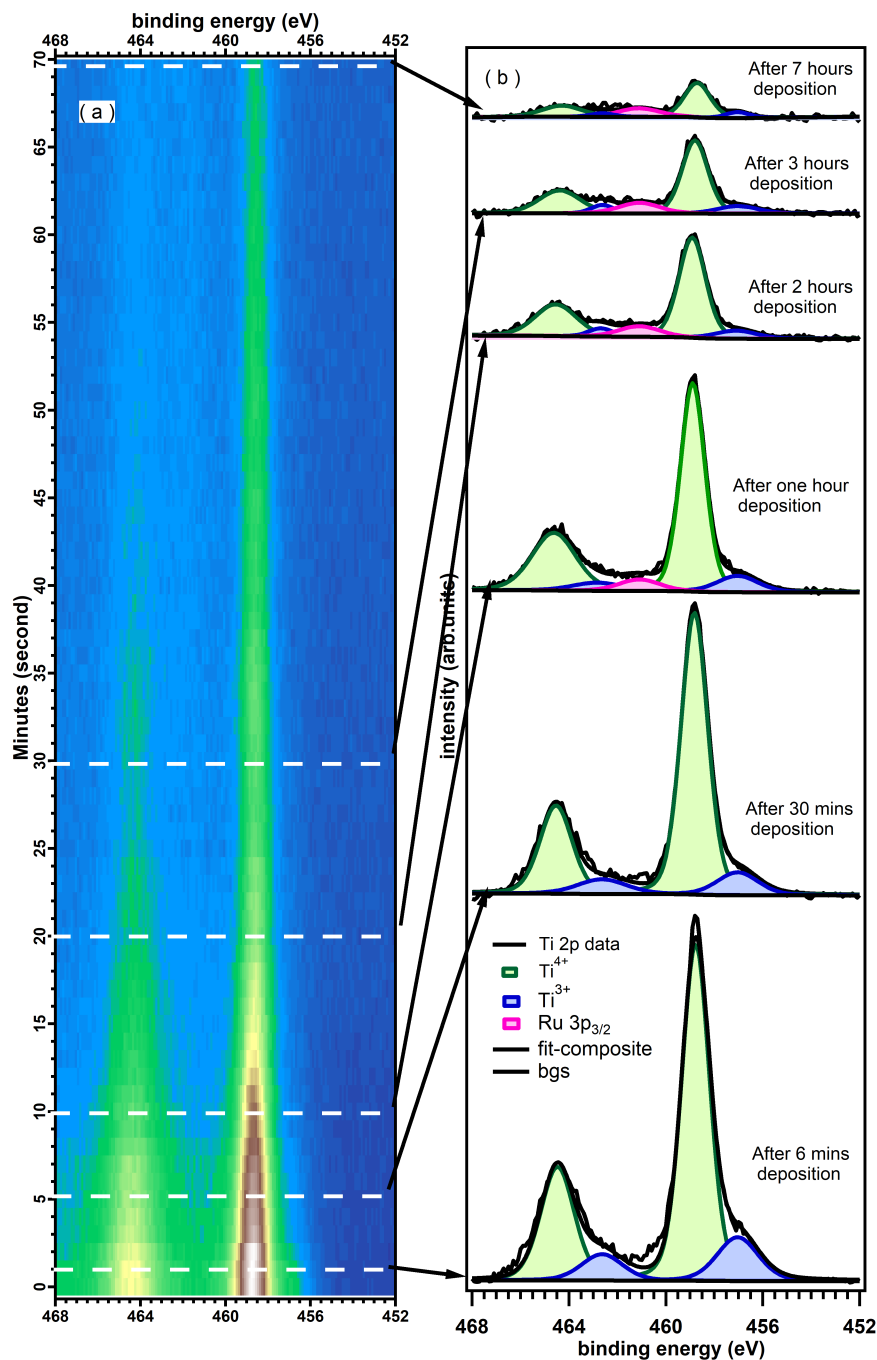


Figure 3.10: The growth stages of the Ti 2p substrate on which N3 molecules were deposited are illustrated, where (a) shows the Ti 2p map, and (b) shows the spectra fitted with time.

3.2. THE EVOLUTION OF N3 FILM THICKNESS ON SINGLE-CRYSTAL RUTILE $\text{TiO}_2(110)$

Figure 3.10 shows the evolution of the Ti $2p$ signal as a function of N3 deposition time. Figure 3.10(a) presents a two-dimensional intensity map with binding energy (eV) on the x-axis and deposition time (minutes) on the y-axis. A significant spectrum is observed at 458.8 eV, corresponding to the Ti $2p_{3/2}$ peak, alongside its spin-orbit linked Ti $2p_{1/2}$ component at 464.3 eV, demonstrating a distinctive splitting of 5.7 eV.

Figure 3.10(b) displays extracted spectra at specified times: 6 minutes, 30 minutes, 1 hour, 2 hours, 3 hours, and 7 hours post-deposition. The spectra at 6 mins and after 30 mins of deposition show the oxidation state of titanium in TiO_2^{+4} and TiO_2^{+3} , when the time is one hours and 2, 3 and after 7 hours, the Ru $3p_{3/2}$ appears at 461.1 eV. As deposition time is increased, the intensities of both Ti^{+4} and Ti^{+3} drop progressively, whilst the Ru $3p$ signal increases. This trend is expected as an increase in N3 molecules over time reduces the substrate signal. The XPS data indicate a gradual decline in the intensity of titanium oxidation states with increasing deposition time. In contrast, the Ru $3p_{3/2}$ signal shows increased intensity.

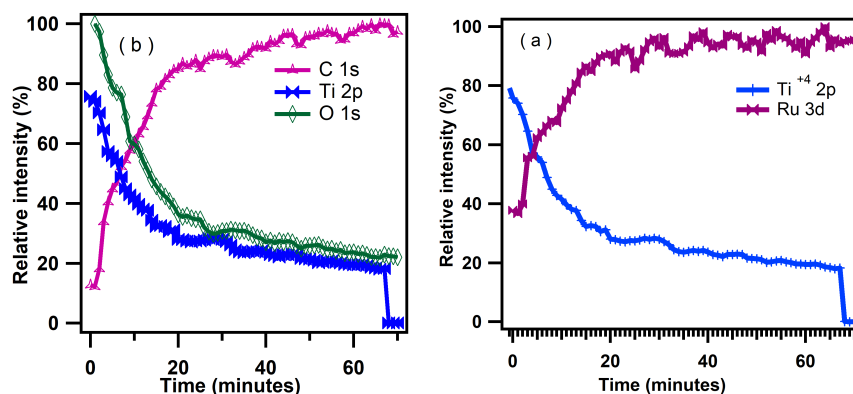


Figure 3.11: (a) The relationship between Ru $3d$ and Ti^{+4} intensities over time of deposition, (b) The relationship between C $1s$, O $1s$ intensities and Ti^{+4} over time of deposition.

Figure 3.11 shows the evolution of Ru $3d$, Ti^{4+} , C $1s$, and O $1s$ relative intensities (%) as a function of deposition time. The left Figure 3.11(a) illustrates two

main trends: the Ti⁴⁺ 2*p* signal (blue line) initially starts at about 75–80%, undergoes a rapid decline during the early deposition stage, and subsequently stabilises near 20–25%. In contrast, the Ru 3*d* signal (purple line) exhibits the opposite behaviour, increasing from approximately 35–40% to nearly 95–100%. The right Figure 3.11(b) presents three elements: oxygen (O 1*s*, green line) begins close to 100% and decreases steadily to about 22–25%, while titanium (Ti 2*p*, blue line) declines from roughly 70–75% to around 18–20%. Finally, carbon (C 1*s*, purple line) increases from approximately 10–15% to almost 100%. These trends indicate that, with increasing deposition time, titanium and oxygen contributions at the surface decrease, whereas carbon and ruthenium increase, consistent with the previously presented figures and confirming the evolution of the surface composition throughout the experiment.

3.2.4 N3 dye sensitized mesoporous TiO₂

Experimental Method

Preparation and coverage calibration of N3 on TiO₂ samples were performed at the University of Nottingham by other members of our group. Coverage was measured by X-ray photoelectron spectroscopy. A monolayer of N3 was prepared by soaking mesoporous TiO₂ electrodes in 5 mg N3 dissolved in 200 ml methanol for one week, then rinsing with methanol and drying under N₂. Multilayer N3 films for synchrotron tests were made by soaking for ten days under inert conditions. Additional physisorbed N3 layers were spin-coated onto silicon wafers for comparison. Resonant photoemission spectroscopy was performed at the FlexPES beamline of the MAX IV synchrotron in Sweden. Full experimental details, including environments and configurations, are documented on the beamline. More details are written by the researcher in this citation [25].

The reason for choosing mesoporous TiO_2 is that it predominantly exists in the anatase phase and possesses a three-dimensional porous network with a high internal surface area, which promotes enhanced dye adsorption. The interconnected structure also facilitates efficient electron transport and electrolyte diffusion, improving light harvesting and charge collection efficiency, and therefore making it an effective photoanode material in DSSCs, as shown in Figure 3.12. In contrast, single-crystal rutile $\text{TiO}_2(110)$ provides a simple, well-defined surface. The subsequent analysis and interpretation of the collected data presented in the following sections are entirely my own work

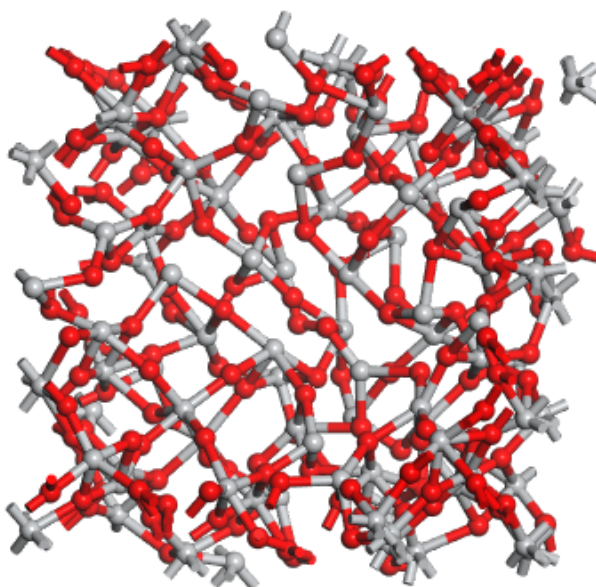


Figure 3.12: Schematic of mesoporous TiO_2 showing its porous surface.

Results and Discussion

Figure 3.13(a) and (b) display the O 1s XPS spectra of the N3 monolayer on mesoporous TiO_2 . The TiO_2 substrate is responsible for the dominant peak, whereas the carboxyl oxygen C=O & COO^- , and C-OH in the bisisonicotinic acid are attributable for the other two smaller peaks. These peaks are located at 530.1, 531.6, and 533.1 eV, respectively. In Figure 3.13 another way of fitting is (b) shows additional peak at 531.3 eV its label as Ti-OH which bonded with bridge TiO_2 that is consist with a peak in above Figure

3.3 which is generated from hydroxyl group (OH) where O atom partial bond with C=O and H atom bonds to the bridge of TiO_2 . Therefore, it consists of terephthalic acid (TPA)/ TiO_2 [70]. Where the TiO–H at 531.3 eV and COO^- at 531.4 eV have similar binding energies, indicating significant surface interaction, especially in the bidentate mode. Usually, bi-isonicotinic bonds to TiO_2 by deprotonating the carboxyl groups [24, 65, 66]. When two oxygen atoms share an electron and are chemically equal. The ratio of COO^- & C=O, and C–OH should be 3:1 if all of the molecules are equally bound to the surface [24]. In this case the ratio of intensity in Figure 3.13 (a) is 2:1 to COO^- & C=O :C–OH while in Figure 3.13(b) is 2:1:1 to COO^- & C=O :C–OH, and TiO–H, respectively. This behaviour suggests that a greater fraction of the carboxyl groups in bi-isonicotinic acid are bonded to the mesoporous TiO_2 surface through deprotonation, or that the molecules are not uniformly bonded across the surface. Alternatively, the C–OH contribution could arise from residual physisorbed species that were not fully removed during sample preparation, rather than exclusively from chemisorbed configurations. The second possibility is that the presence of C–OH in mesoporous titania suggests two distinct bonding geometries, with bidentate bridging advantageous for the 101 surface and monodentate bonding stable for the 001 surface [67]. This feature may be due to altered bonding geometry in mesoporous titania, which may blend 101 and 001 structures [25].

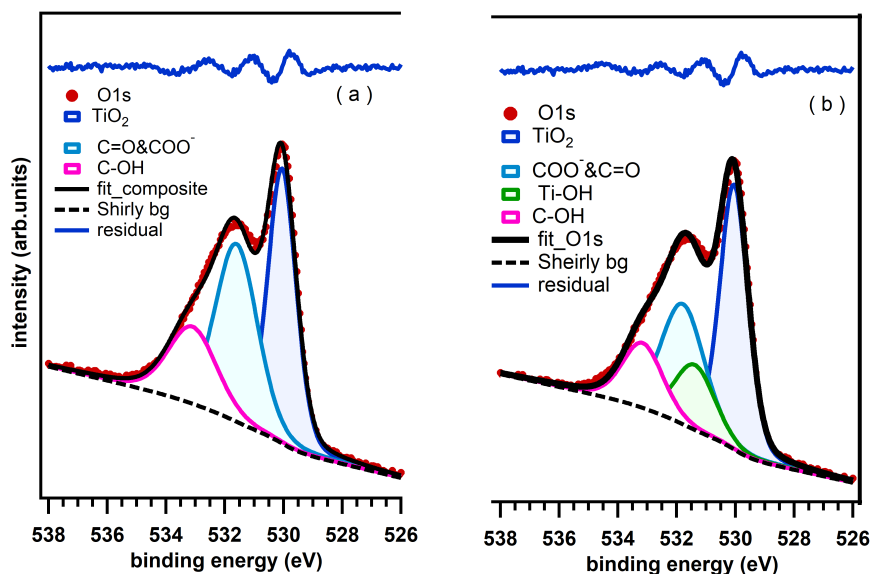


Figure 3.13: O $1s$ XPS spectra of a mesoporous TiO_2 –N3 monolayer. The dashed black line indicates the Shirley background. With a photon energy of 600 eV, both spectra were taken at normal emission (NE).

Figure 3.14 displays the five peaks in the C $1s$ XPS at 280.8, 284.7, 285.7, 286.5, and 288.5 eV, as listed in Table 3.3. Specifically, the peak at 280.8 eV corresponds to Ru $3d_{5/2}$, 284.7 eV to C–C, 285.7 eV to C–N, 286.5 eV to the thiocyanate group, and 288.5 eV to the carboxyl (COOH) group. The Ru $3d$ spectrum exhibits spin–orbit splitting into the $3d_{5/2}$ and $3d_{3/2}$ components, with the peak at higher binding energy (~ 285 eV) corresponding to the Ru $3d_{3/2}$ contribution overlapping with the C $1s$ region. The strong C $1s$ signal comprises C–C (C 2, 3, 4 in pyridine), C–N (C 1, 5 in pyridine), and C in the thiocyanate group. The intensity ratio between these peaks is 6:4:1:2, respectively [24, 78]. The binding energies in this study match those for thin coverage of N3 on TiO_2 NPs (see Subsection 3.2.5). As will be shown later in this chapter, the behaviour observed for N3 on nanoparticles is consistent with this interpretation. It is similar to the thick coverage seen in the previous study (see Figure 3.5). It also matches the previous study of the N3 dye on Au(111) [31, 79], supporting that N3 is adsorbed on the surface of mesoporous TiO_2 .

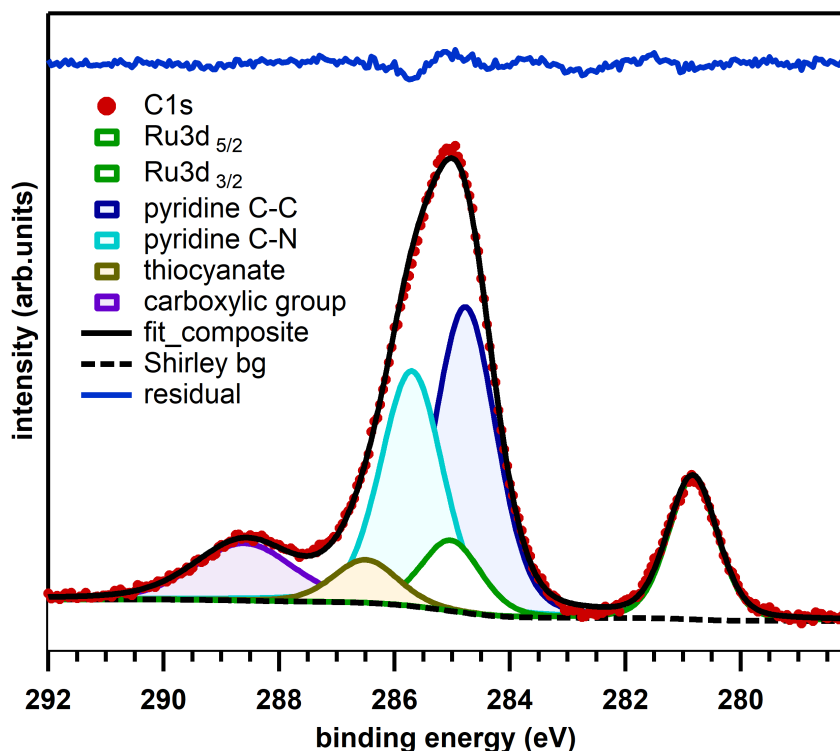


Figure 3.14: XPS spectra of N3 monolayer on a mesoporous TiO_2 C 1s. The dashed black line represents Shirley's background. The spectrum was acquired at normal emission (NE) using a photon energy of 600 eV.

Figure 3.15 shows S 2*p* photoemission spectroscopy of N3 on mesoporous TiO_2 measured using $h\nu = 225$ eV. S 2*p* is a doublet state with spin-orbit splitting of 1.16 eV [74]. Two distinct chemical environments are observed for the S atoms. The lower binding-energy component at 161.8 eV is attributed to sulphur species that are not directly bonded to the TiO_2 surface, whereas the higher binding-energy peak at 162.7 eV indicates sulphur atoms interacting with the TiO_2 substrate. These binding energies are consistent with previous reports for N3 adsorbed on rutile TiO_2 [24] and with the results discussed in Figure 3.4. This has already been suggested for N3 monolayers on nanostructured TiO_2 that have been prepared ex situ [66].

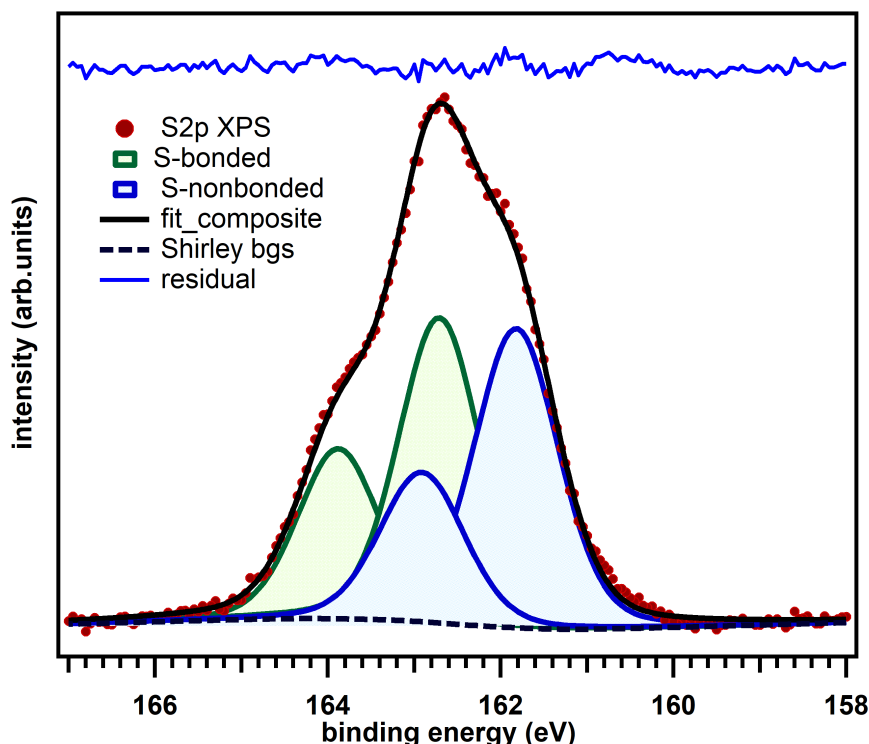


Figure 3.15: XPS spectra of N3 monolayer on a mesoporous TiO_2 S 2p. The dashed black line represents Shirley's background. The spectrum was acquired at normal emission (NE) using a photon energy of 225 eV.

Figure 3.16 shows the N 1s XPS spectrum. There are two peaks, corresponding to pyridine at 400 eV and thiocyanate at 397.8 eV, with an intensity ratio of 2:1.

3.2.5 N3-dye-sensitized TiO_2 nanoparticles

Experimental Method

The preparation was made in our lab at the University of Nottingham by mixing TiO_2 (21 nm) and the N3 dye complex, both from Sigma-Aldrich and Merck. The concentration of TiO_2 solution was 0.1 wt% (0.015 g of TiO_2 and 15 g of ethanol). This study included the preparation of N3 dye-sensitised TiO_2 nanoparticles (NPs) using two deposition techniques. In the case of the thinnest coverage, the TiO_2 NPs were deposited in situ via electrospray deposition (ESD) as described in Chapter 2. For thin, medium, and thick coverings, the samples were prepared ex situ by drop-casting. The sensitisation

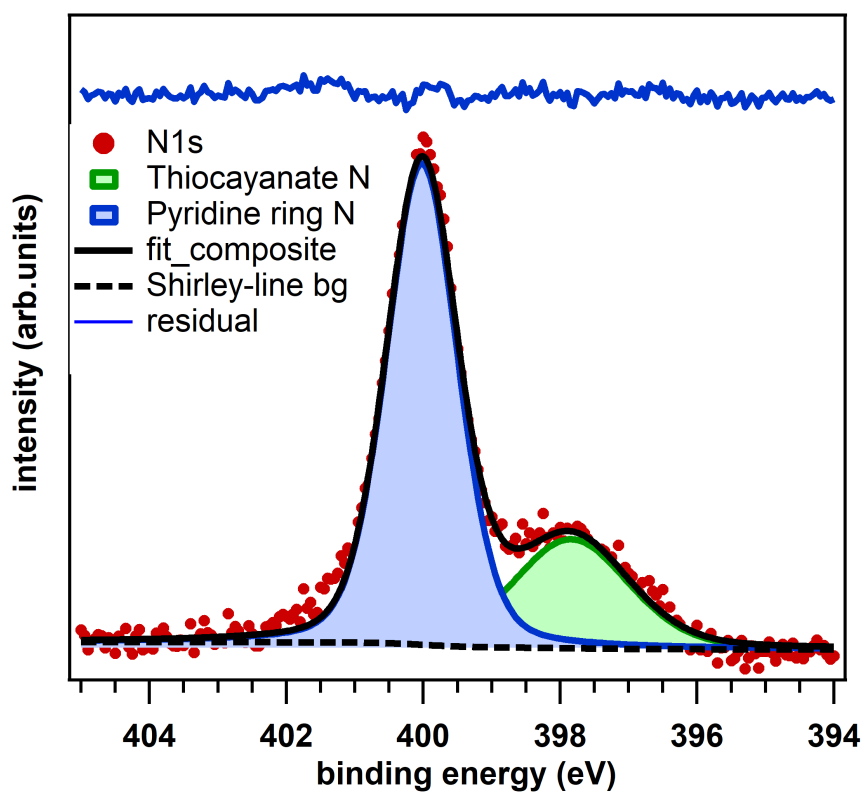


Figure 3.16: N 1s XPS spectrum of monolayer on a mesoporous TiO_2 . The Shirley background was removed. It is measured using a photon energy at 600 eV.

3.2. THE EVOLUTION OF N3 FILM THICKNESS ON SINGLE-CRYSTAL RUTILE TiO₂(110)

Table 3.3: Peak BEs (eV) according to N3-mesoporous TiO₂, where all spectra are calibrated to O 1s = 530.05 eV.

PEs	Peak	BEs (eV)
O 1s	TiO ₂	530.1
	COO ⁻ & C=O	531.6
	C–OH	533.1
	Ti–OH	531.3
C 1s	R 3d	280.8
	C–C	284.7
	C–N	285.7
	NCS	286.5
	COOH	288.5
N 1s	Pyridine	400
	thiocyanate	397.8
S 2p	S–nonbonded	161.8
	S–bonded	162.7

with N3 dye was conducted under the same conditions described in Chapter 2. The beamline and the Surface and Material Science (SMS) end station on the FlexPES beamline at the Swedish MAX IV synchrotron radiation facility were used for measurements.

FlexPES is on the 1.5 GeV storage ring. It uses a collimated planar grating monochromator and a planar undulator to send out photons with energies between 40 and 1500 eV. These photons may either be concentrated into a 65×10 Mm spot at the SMS branch sample site, or they can be defocused to produce a larger size of 1.0×0.4 mm². The experimental station is outfitted with a homemade partial electron yield (PEY) microchannel plate (MCP) detector for X-ray absorption measurements and a Scienta SES-2002 hemispherical analyser for photoelectron spectroscopy (PES), which is mounted at a 40-degree angle from the incident photon beam.

Measurements were done with the sample facing the analyser at normal emission [80]. Binding energy (BE) scales were calibrated using X-ray photoelectron spectroscopy (XPS), measured at $h\nu = 650$ eV, by setting the Ti $2p_{3/2}$ peak to 458.8 eV [69]. Each spectrum of molecular elements was calibrated to Ti $2p_{3/2}$. By measuring the kinetic energy difference of photoemission peaks produced by first and second-order light, it was determined that photon energy scales and the repeatability of beamline energy were accurate to within 50 meV. Peak fitting of the XPS data was performed using a pseudo-Voigt line shape with a fixed Gaussian–Lorentzian mixing parameter of 0.3. Before curve fitting, a linear or Shirley background was eliminated. The captions of the relevant figures contain information on these factors. NEXAFS spectra were recorded in partial electron yield mode using the hemispherical electron analyser, by monitoring the photoelectron signal while scanning the photon energy across the s 1s, C 1s, and O 1s absorption edges.

Results and Discussion

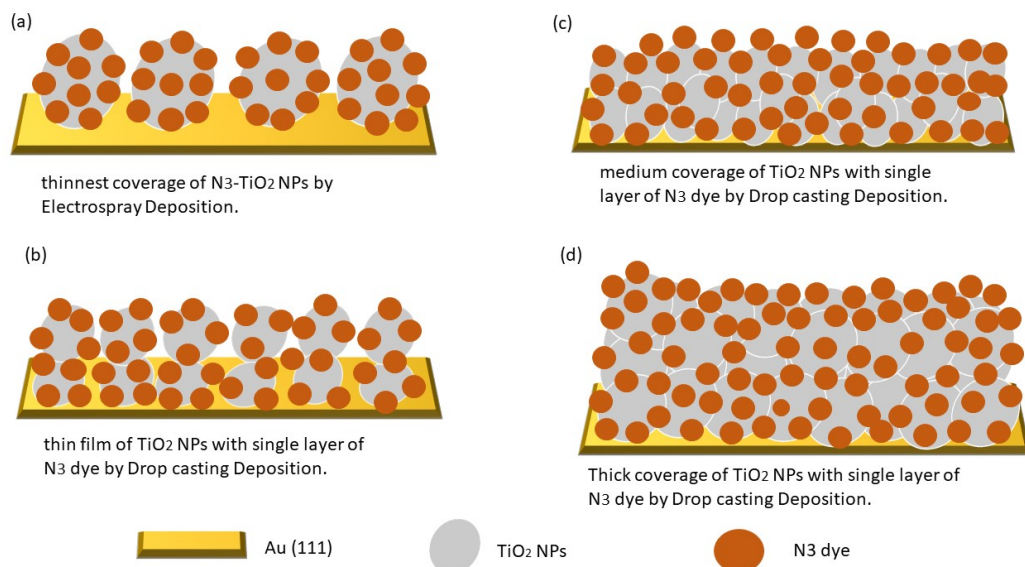


Figure 3.17: Schematic illustration of the evolution of N3-sensitised TiO_2 nanoparticle coverage, highlighting the change in surface packing density and dye accessibility from ESD-deposited monolayers to drop-cast thick films.

This study employs XPS to examine the interactions between N3 dye molecules and TiO_2 NPs, and NEXAS to explore the electronic structure of N3 on the TiO_2 NPs, in addition to RPES to examine the charge-transfer lifetime. The samples and binding energies of the peaks are provided in Tables 3.4, 3.5, 3.6, and 3.7. They were prepared by electrospray deposition (ESD) and drop casting, respectively.

Figure 3.18 shows a Ti $2p$ photoelectron spectrum of the N3- TiO_2 NPs. There are two Ti states: the highest, Ti $2p_{3/2}$, at 458.8 eV, and the lowest, Ti $2p_{1/2}$, at 464.4 eV. It is a doublet state with a spin-orbit splitting of 5.7 eV [76]. Thus, this led to Ti^{+4} oxidation state. The lack of Ti^{+3} features suggests that the oxide was produced by chemical synthesis rather than sputtering or annealing, as these methods typically introduce defects that give rise to Ti^{+3} states.

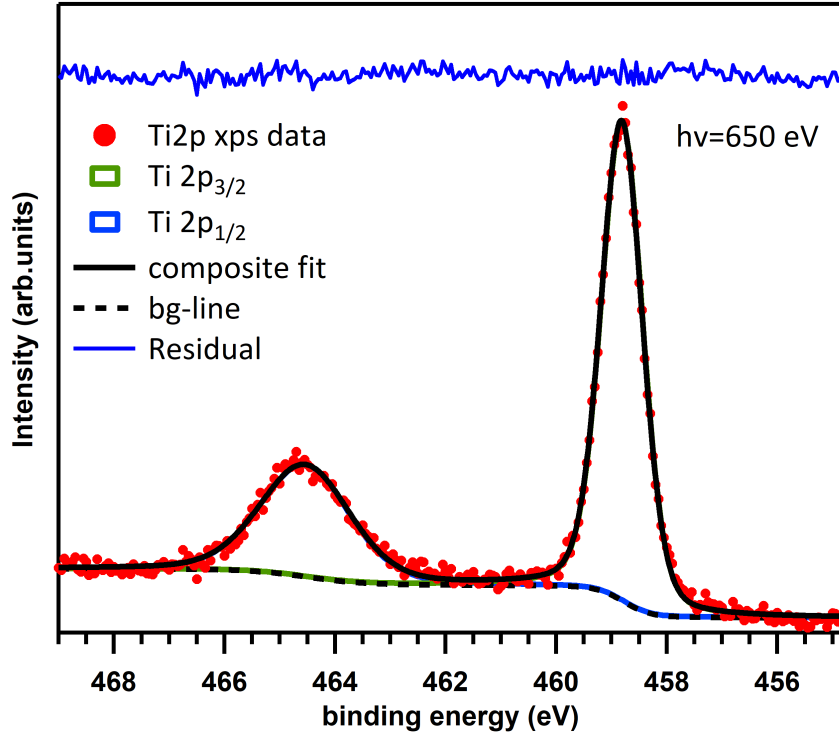


Figure 3.18: Ti $2p$ core-level Spectrum of N3 on a TiO_2 NPs. The black line represents the fit, and Shirley’s background has been applied in the fit measured using $h\nu = 650$ eV.

Figure 3.19 shows the O $1s$ XPS spectra of thin, medium, and thick coverage of N3– TiO_2 NPs deposited by drop casting; (b) the thinnest coverage of N3– TiO_2 NPs that ESD deposited; and (c) the O $1s$ of bulk N3 without TiO_2 . In Figure 3.19, the distinctive peak corresponds to lattice oxygen $\text{O}_{\text{lattice}}$ in TiO_2 , which expresses the amount of TiO_2 in each coverage as shown 3.19(a), from thin coverage to thick at BE 530 eV, which is expected. However, in the thinnest ESD-deposited coverage in figure 3.19(b), a relatively high TiO_2 signal is observed compared to the thin drop-cast sample. This suggests that the signal is dominated by exposed TiO_2 nanoparticles rather than a continuous molecular layer. In such low coverage, individual nanoparticles or partially uncovered regions can contribute significantly to the detected intensity. In contrast, at thick coverage, the TiO_2 nanoparticles form a more continuous, mixed layer.

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The other peaks are attributed to O in the N3 molecule, which is COO⁻, Ti-OH, C=O, and C-OH. These peaks are observed at BEs of 531.4, 531.3, 532.4, and 533.5 eV for thick, medium, thin, and thinnest coverage, respectively, while C=O and C-OH in thin and thinnest coverage are shifted to lower BEs at 532 and 533.1 eV, respectively. The reason for this shift is that the Oxygen atom can contact the Au surface. The COOH group in bi-isonicotinic acid is usually bonded to TiO₂ by deprotonation [24, 65, 66], where two oxygen atoms share an electron and are chemically equivalent. The ratio between COO⁻, C=O, and C-OH is estimated to be 2:1:1 if all the molecules are equally bound to the surface. But in our case, the calculated ratio of the intensity of COO⁻, C=O, and C-OH from experimental data is 1.8:1:1 ($\pm$ fitting uncertainty) for each coverage except thick coverage, which is 2.1:1:1. This could happen if the COO⁻ bonded to the bottom of TiO₂ NPs or could touch the Au surface, while the thick coverage is evidence that the COO⁻ bonded to TiO₂ in an equivalent way. The peak at 531.3 eV is generated from the hydroxyl group (OH), where the O atom partially bonds with C=O to be COO⁻, and the H atom bonds to the bridge of TiO₂. Thus, it consists of terephthalic acid (TPA)/TiO₂ where H bonds to TiO₂ to be Ti-OH at 531.3 eV [70].

Figure 3.19(c) shows the O 1s photoelectron spectra of bulk N3 on Au without TiO₂ measured using $h\nu = 650$ eV. The spectrum shows two separate peaks at 531.2 and 532.8 eV. There are two distinct chemical environments associated with the carbonyl C=O and hydroxyl C-OH groups, respectively. The hydroxyl oxygen does not deprotonate, so the ratio between them is 1:1, which is identical to [31]. However, this is the opposite of the adsorption of N3 on TiO₂ [24]. It presents a 3:1 peak ratio because two of the carboxylic groups were deprotonated. Therefore, on Au(111), the carboxyl groups of N3 remain protonated, resulting in weak surface binding. In contrast, deprotonation on TiO₂ enables strong bonding. Hence, the carboxylic acid in N3 does not bond

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to the Au(111) substrate. The Table 3.4 shows a summary of binding energies for the O 1s spectrum for each coverage.

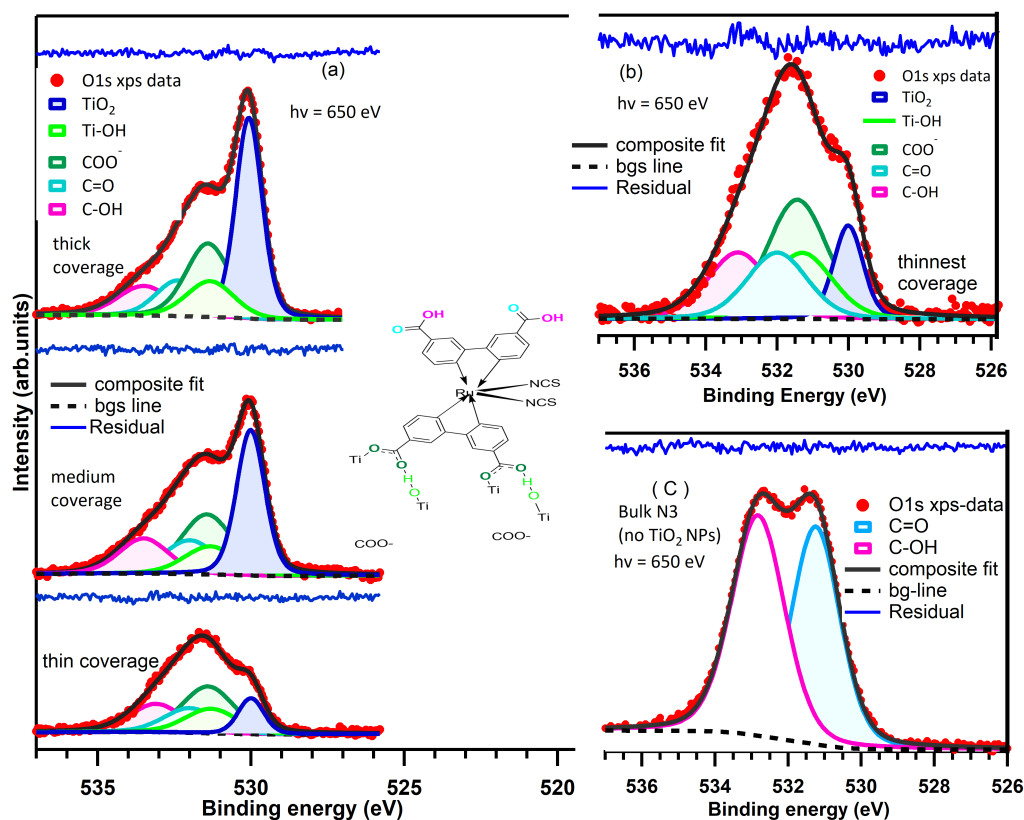


Figure 3.19: BEs (eV) to the thin, medium and thick coverage of N3-TiO₂ nanoparticles by drop casting where all spectra are calibration to Ti 2p at 458.8 eV, which they presented (a), and (b) represent to O 1s by ESD to the thinnest coverage of N3-TiO₂ in addition to (c) shows the bulk N3 without TiO₂ NPs spectra.

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Table 3.4: BEs (eV) to the thick coverage of N3–TiO₂ NPs by drop casting and the bulk of N3 without TiO₂ NPs, in addition to the thinnest coverage by ESD where all spectra calibration to Ti 2p_{3/2} at 458.8 eV. Taking into account that thin coverage is matched to the thinnest coverage in BEs, and medium is matched to the thick coverage as well.

O 1s	Thinnest coverage	Thick/medium coverage	N3/Au(111)
	BE (eV)	BE (eV)	BE (eV)
TiO ₂	530.0	530.0	
COO [−]	531.4	531.4	
TiO–H	531.3	531.3	
C=O	532.0	532.4	531.2
C–OH	533.1	533.5	532.8

Figure 3.20(a) shows the S 2p photoelectron spectra for thin, medium, and thick N3–TiO₂ nanoparticle coverages deposited by drop casting and measured at $h\nu = 380$ eV. The S 2p signal exhibits the expected spin–orbit doublet with a splitting of 1.18 eV [74]. Four chemically distinct S– related doublets are required to achieve optimal fitting for all coverages, and their binding energies are summarised in Table 3.5.

The lowest binding energy component at 160.8–160.9 eV is assigned to S–Au bonding. This contribution is most intense at thin coverage and decreases systematically with increasing coverage, indicating that sulphur atoms preferentially interact with the Au(111) substrate at low coverages. The narrow line width of this component (average FWHM ~ 0.4 eV) suggests a well-defined, uniform chemical environment. This assignment is consistent with the previous XPS study of atomic sulphur on Au(111), which identified a low-binding-energy doublet associated with sulphur occupying threefold hollow sites on the Au surface [81].

A second component appears at higher binding energies, centred at 161.6 eV for thin coverage and shifting to 162.1 and 162.3 eV for medium and thick coverages, respectively. This feature is significantly broader (FWHM ~ 1.1 – 1.3 eV) and persists across all coverages, indicating contributions from multiple

sulphur chemical environments with similar but unresolved binding energies. Based on comparison with previous studies [24], this component is attributed primarily to nonbonded sulphur, with possible minor contributions from sulphur weakly interacting with Au or neighbouring sulphur atoms. The increase in binding energy with coverage suggests reduced screening and a changing local chemical environment as TiO₂ nanoparticle coverage increases.

The component at 163.1 eV is assigned to S–TiO₂ bonding, consistent with reported binding energies for sulphur interacting with Ti rows on TiO₂ surfaces. This contribution becomes progressively more dominant from thin to thick coverage, reflecting the increasing availability of TiO₂ surface sites and enhanced sulphur–TiO₂ interaction at higher nanoparticle loadings. The linewidth of this component narrows at medium and thick coverages, indicating a more uniform bonding environment compared with thin coverage.

At higher binding energies (~ 164.5 – 164.7 eV), a weak and broad doublet is observed and assigned to oxidised sulphur species (S–O lattice). The intensity of this component increases with TiO₂ coverage, suggesting that it is associated with sulphur–oxygen interactions either at the TiO₂ surface or formed during sample preparation. Given its relatively low intensity compared with the other components, this contribution represents a minor sulphur species.

Figure 3.20(b) presents the S 2*p* spectrum for the thinnest N3–TiO₂ coverage deposited by electrospray deposition (ESD). The binding energies of all components closely match those observed for the thin drop-cast film, indicating similar chemical states. However, the relative intensities differ: the S–Au contribution is reduced, while the S–TiO₂ component is enhanced. This indicates that, for ESD deposition, sulphur preferentially bonds to the sidewalls and surfaces of TiO₂ nanoparticles rather than to the Au(111) substrate. This behaviour is consistent with the O 1*s* results in figure 3.19, which indicate a slightly higher effective TiO₂ presence in the thinnest ESD coverage.

Overall, the evolution of S 2*p* components with coverage reflects a transition from substrate-dominated sulphur bonding S–Au at low coverage to nanoparticle-

3.2. THE EVOLUTION OF N3 FILM THICKNESS ON SINGLE-CRYSTAL RUTILE $\text{TiO}_2(110)$

dominated bonding S– TiO_2 and S–O lattice at higher coverage, with non-bonded sulphur present across all regimes.

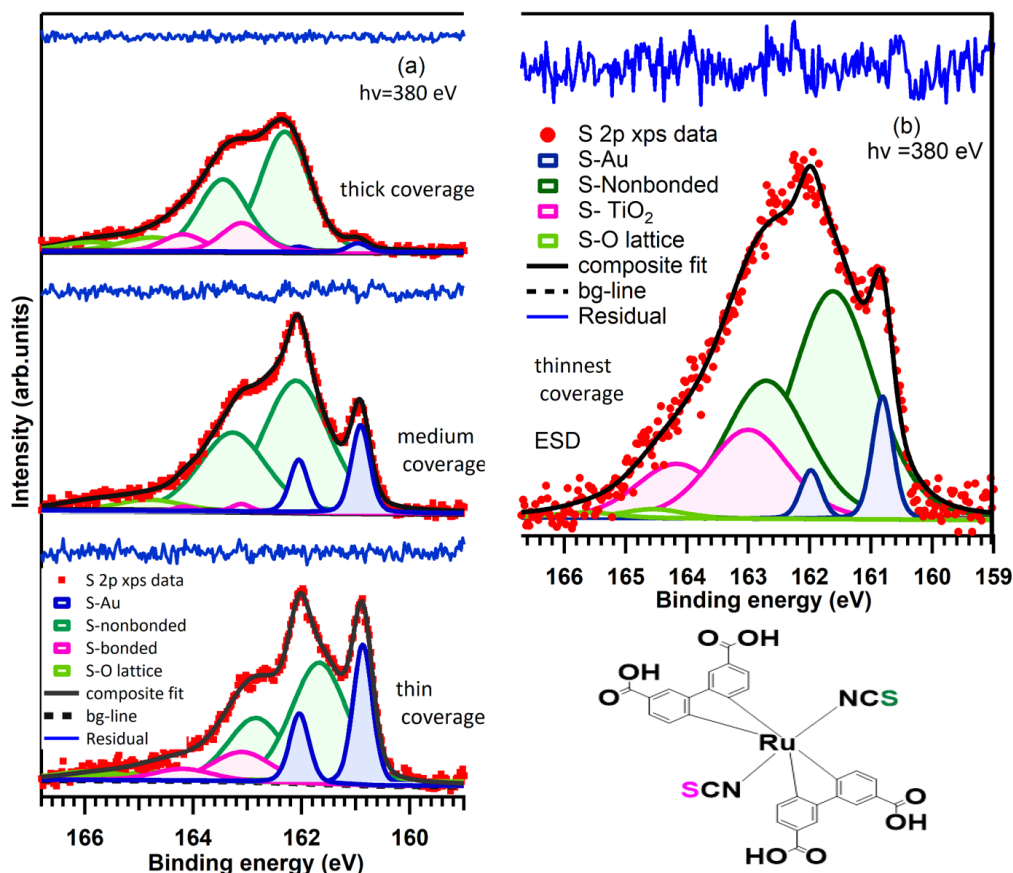


Figure 3.20: S 2*p* core-level Spectra of N3 on a TiO_2 NPs to a thick, medium and thin coverage by Drop casting (b) for S 2*p* spectrum deposited by ESD. The dashed black line represents Shirley's background measured using $h\nu = 380$ eV.

Table 3.5: Parameters of the XPS component BEs for S 2*p* for the thinnest and thickest, where the thin is matched to the thinnest and the medium matched thick coverage.

S 2 <i>p</i>	Thinnest N3– TiO_2 NPs ESD	Thick N3– TiO_2 NPs Drop Casting
	BE (eV)	BE (eV)
S–Au	160.8	160.9
S–nonbonded	161.6	162.3
S– TiO_2	163.1	163.1
S–O _{lattice}	164.5	164.5

3.2. THE EVOLUTION OF N3 FILM THICKNESS ON SINGLE-CRYSTAL RUTILE TiO₂(110)

Figure 3.21(a,b,c) show the C 1s and Ru 3d photoelectron spectra of thin, medium, and thick coverages by drop casting of the N3–TiO₂ NPs, as well as the thinnest coverage of N3–TiO₂ NPs by ESD in addition to bulk N3 without TiO₂, respectively. Both coverages were measured at a photon energy of 380 eV. The peak at 280.9–281.3 eV, shown in table 3.6, corresponds to Ru 3d_{5/2}, while the Ru 3d_{3/2} component appears at a binding energy 4.2 eV higher [75]. The remaining C 1s spectra have been curve fit using four peaks except 3.21(b), which has just three peaks. By comparing these studies [24, 31, 79], the most intense peak in the spectrum at 285 eV is assigned to the C atom in the pyridine ring. That is where you can get to C in the pyridine ring; two of them surround the N atom (atoms 1 and 5), and those that are not neighbours to the N atom (atoms 2, 3, and 4). These peaks are located at 284.9 eV and 284.6 eV at the lowest (thinnest, medium, and thin) coverages, respectively, while the highest coverages, such as thick and bulk N3 with no TiO₂, were 285.4 eV and 286.2 eV, respectively. The peak is located at $\approx$ 286.6 eV for the lowest coverage, while the highest coverage is $\approx$ 287.1 eV due to the thiocyanate group (NCS). In addition to the last peak at 288.8 eV for all coverages except bulk N3 (289.2 eV), this peak is due to carboxyl groups (COOH). Based on the calculated N3 molecule ratio, which is pyridine C–C (2,3,4): pyridine N–C (1,5): thiocyanate (NCS): carboxyl, it is 6:4:1:2, respectively. The relative contributions of pyridine, thiocyanate, and carboxyl components vary slightly with coverage, but the overall trends are already evident in Figure 3.21. Pyridine-related carbon decreases gradually with increasing coverage, while the thiocyanate and carboxyl contributions remain comparatively stable with only minor variations. These small changes in relative intensity and binding energy suggest that N3 molecules are present across all coverages, with differences likely arising from adsorption at different TiO₂ nanoparticle surface sites.

3.2. THE EVOLUTION OF N3 FILM THICKNESS ON SINGLE-CRYSTAL RUTILE $\text{TiO}_2(110)$

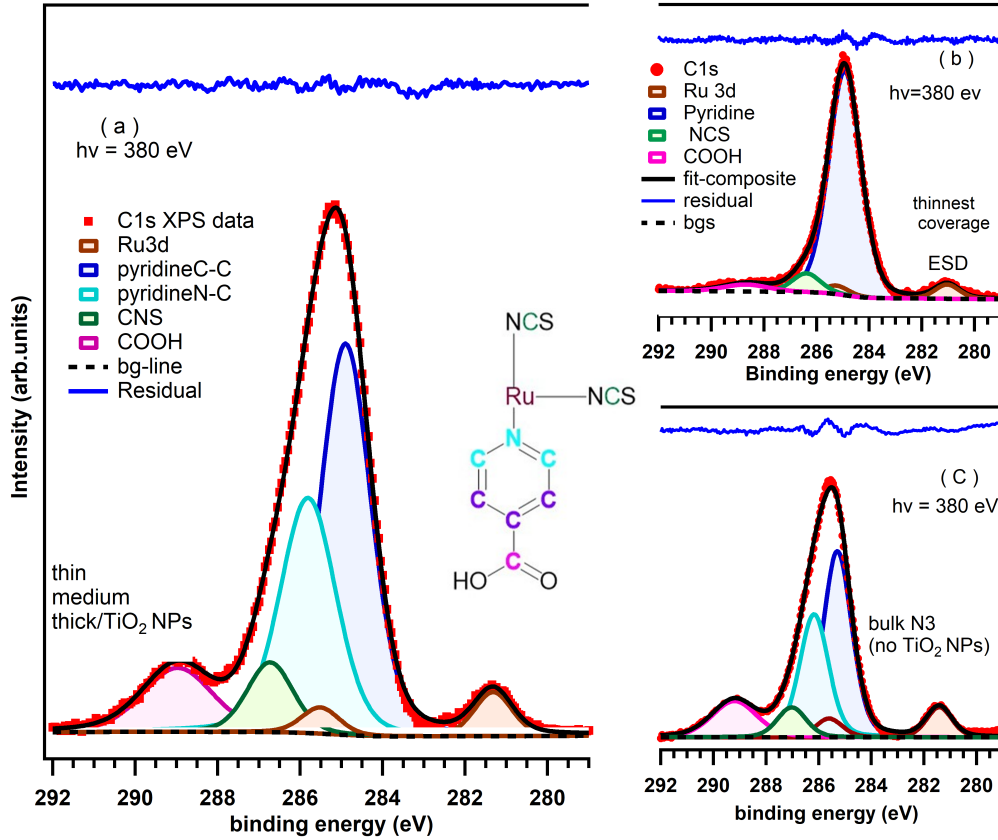


Figure 3.21: C 1s core-level spectra of N3-TiO₂ nanoparticle samples measured at $h\nu = 380$. (a) Thin, medium, and thick N3-TiO₂ nanoparticle coverages deposited on Au(111) by drop casting, together with the fitted components assigned to pyridine C-C, pyridine N=C, NCS, and COOH species, the composite fit, background, and residual. (b) The thinnest N3-TiO₂ nanoparticle coverage prepared by (ESD), shown with the corresponding peak deconvolution and fitting components.

Table 3.6: Parameters of the XPS component BEs for C 1s for the thinnest coverage and thick coverage, where the thin is matched to the thinnest and medium matched thick coverage, in addition to bulk N3/Au(111).

	Thinnest coverage	thick coverage	bulk N3
Ru 3d	280.9	281.3	281.4
C-C	284.9	285.4	285.3
C-N		286.2	286.2
NCS	286	287.2	287.2
COOH	288.6	288.9	289.2

Figure 3.22 shows the bottom spectrum of the N $1s$ photoelectron of the N3– TiO_2 NPs for thin, medium, and thick drop casting deposition, and the above spectrum shows the spectrum of bulk N3 no TiO_2 NPs, both measured using $h\nu = 500$ eV. N3 is composed of pyridine and thiocyanate N atoms in a ratio of 4 (pyridine):2 (thiocyanate) N atoms. There are the same ratios for each coverage; these ratios are 2:1 for thin and medium, as shown here, further indicating that the molecules arrive at the surface in their entirety.

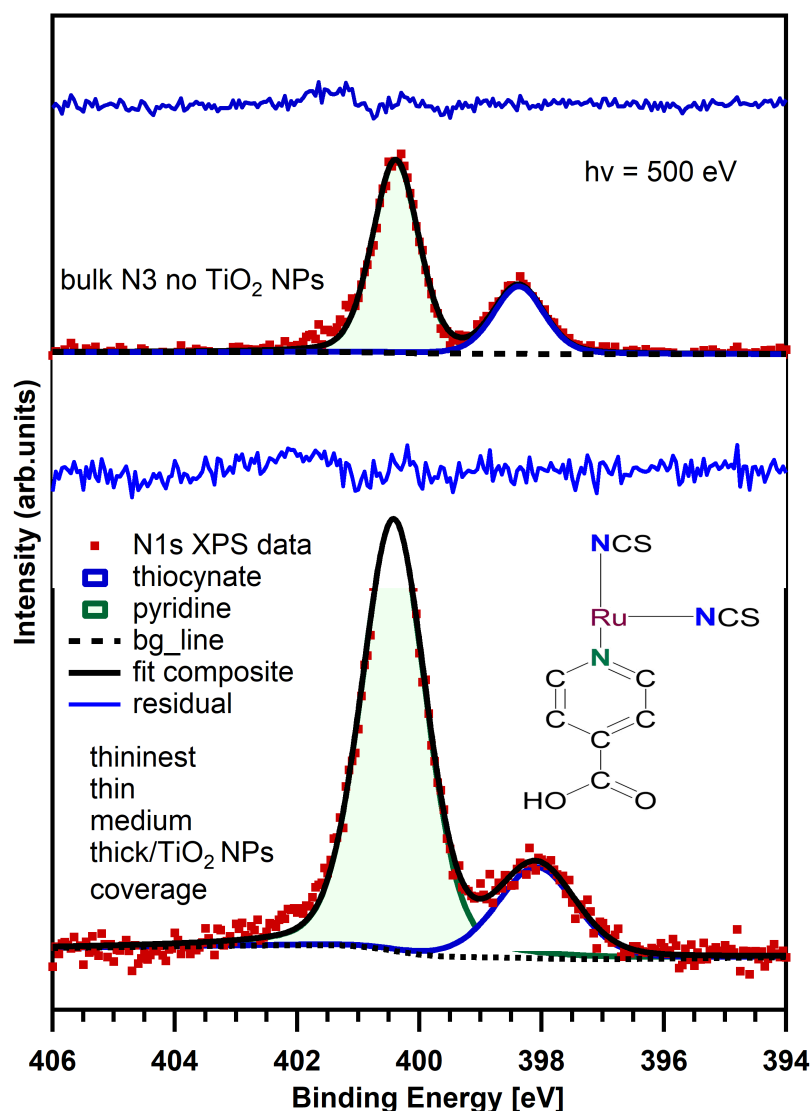


Figure 3.22: N $1s$ core-level spectra of N3– TiO_2 nanoparticle samples measured at $h\nu = 500$ eV. The bottom panel shows thin, medium, and thick coverage samples prepared by drop casting on TiO_2 nanoparticles. The upper panel shows bulk N3 without TiO_2 nanoparticles, with the binding energy referenced to Ru. The dashed black line represents the Shirley background, and the coloured components correspond to pyridine, thiocyanate (NCS), and the composite fit.

Table 3.7: The BEs of N $1s$ to thick, medium, thin and thinnest coverage by Drop casting and the bottom spectrum shows the spectrum of the bulk of N3/Au(110), which was measured using $h\nu = 500$ eV.

N $1s$	thinnest to thick coverage	bulk N3/Au
NCS	398.1	398.3
Pyridine	400.3	400.3

3.3 Electronic structure

3.3.1 Density of states (DoS)

In a DSSC, electrons from high-occupied molecular orbitals in the dye are photo-excited to unoccupied molecular orbitals. For subsequent electron injection into the TiO_2 substrate, the dye's previously unoccupied level involved in the transfer must align with a range of states in the TiO_2 conduction band. The spectra showing the occupied and unoccupied states of the N3 monolayer have been aligned on the same binding energy scale, as detailed in Chapter 2. This image is essential for clarifying the charge transfer mechanisms that may occur in the N3/ TiO_2 dye-sensitised solar cell model. [79, 82, 83]. Interestingly, the conduction band edge of the substrate is in proximity to the Fermi level, suggesting only slight band bending.

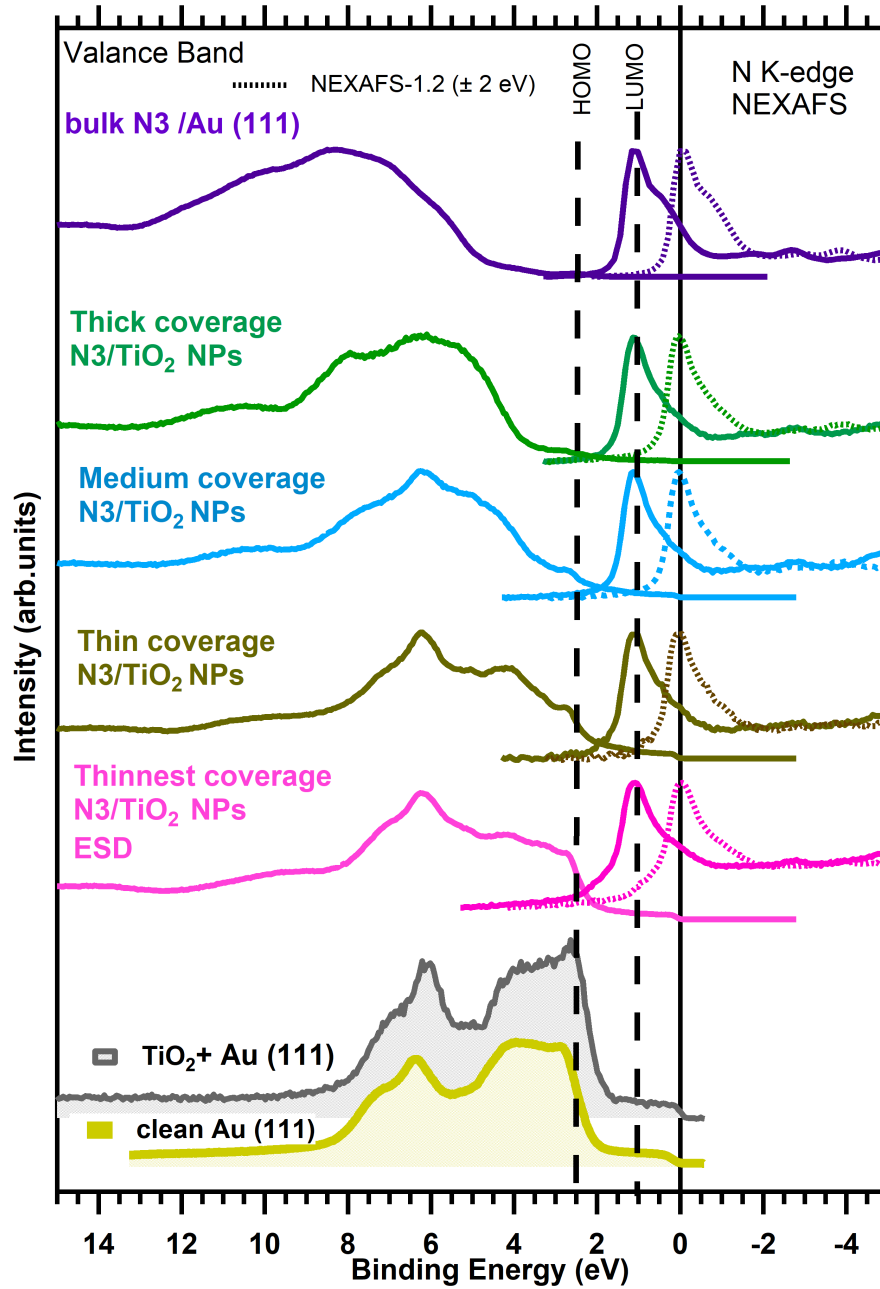
3.3.2 N3/TiO₂ NPs

Figure 3.23: Valence-band photoemission and N K-edge NEXAFS spectra of TiO₂+Au(111), clean Au(111), and N3/TiO₂ NP samples at different coverages. Solid lines show the original NEXAFS spectra, while dashed lines are rigidly energy-shifted to align the N3 HOMO–LUMO gap. The dashed vertical line marks the HOMO position and the solid vertical line the LUMO resonance.

Figure 3.23 shows many spectra starting with clean gold Au(111). A combination of TiO₂ and Au(111), and the rest of the spectra represent the valence photoemission of different coverages of N3 on TiO₂ NPs. The spectrum above corresponds to bulk N3 on Au(111), measured using Near Edge X-ray Absorption Spectroscopy (NEXAS). The data are presented on a common binding energy scale for comparison. This is what we get when we subtract the N 1s core-level binding energy from the photon energy scale of N 1s near-edge X-ray absorption spectroscopy. Some other sources [51] provide more detail on combining valence photoemission spectra with near-edge X-ray absorption spectra. The binding energies to LUMO 0 and LUMO+1 are at BE $\approx$ 1.1 eV and BE $\approx$ 0.3 eV for the thinnest coverage that was deposited by ESD. The LUMO 0 and LUMO +1 are at BE $\approx$ 1.03 eV, BE $\approx$ 0.03 eV, BE $\approx$ 1.1 eV, BE $\approx$ 0.3 eV, and BE $\approx$ 1.4eV, BE $\approx$ 0.3 eV, for the thin, medium, and thick coverage of N3/TiO₂ NPs, respectively. Their BEs indicate that they are located lower than the Fermi level and strongly overlap with the conduction band of TiO₂ NPs.

LUMO+2 and LUMO+3, on the other hand, are above the Fermi level. The HOMO state is not clear in thick coverage at 2.3 eV, so the HOMO at the bulk of N3 on Au(111) is referenced. The dashed light line to NEXAFS is shifted to align with the optical HOMO-LUMO gap. This correction accounts for the excitonic effect arising from the presence of a core hole and an excited electron, which artificially lowers the apparent energy of the LUMO relative to its position in a real operating device. The magnitude of the energy shift is determined by aligning the NEXAFS LUMO resonance with the optical HOMO–LUMO gap, obtained from the measured HOMO position in valence-band photoemission and the optical absorption onset. This shift compensates for the core-exciton binding energy that lowers the apparent LUMO position in NEXAFS. This approach is based on the assumption that core excitons significantly affect the LUMO position, whereas valence excitons do not. Sim-

ilar effects of core-hole excitons on LUMO energies have been systematically reported in the literature [84]. The purple spectrum of bulk N3 on Au(111) shows the HOMO peak at 2.3 eV, as seen in earlier studies [31, 63]. It becomes a reference because the HOMO is not clearly visible in UPS spectra for the thinnest, thin, medium, and thick coverage of N3 on TiO₂ NPs. The LUMO-derived states are observed at low binding energies and lie above the Fermi level, consistent with their overlap with the TiO₂ conduction band. LUMO+2 and LUMO+3 have been located above the Fermi level, which allows the electrons in the excited states to transfer to the conduction band of TiO₂ NPs. The light purple is the NEXAFS shifted to -1.2 eV to align the optical HOMO-LUMO gap. In an actual solar cell device, this energy overlap facilitates electron injection from the LUMO of the N3 dye complex onto the substrate. There is a core exciton in the NEXAFS, which means that the LUMO and LUMO+1 of the core-excited systems are inside the substrate band gap. This stops charge transfer for these orbitals. In the next section 3.4, excited electrons in the LUMO serve as a guide, allowing the study of electron injection from the unoccupied levels above the conduction band edge [54, 85].

3.3.3 N3 on mesoporous TiO₂

Figure 3.24 displays a combination of the valence-band photoemission spectrum and the N K-edge X-ray absorption (NEXAFS) spectrum for multilayer N3 on mesoporous TiO₂, shown on a common binding-energy scale. This is achieved by subtracting the N 1s core-level binding energy from the photon energy scale of the N 1s NEXAFS spectrum. The blue spectrum represents the valence photoemission of the N3 dye, where the HOMO peak is located at BE = 2.3 eV, and LUMO0 is located at BE = 0.8 eV. The light purple line is XAS shifted by -0.7 eV to align with the optical HOMO-LUMO energy gap derived from the HOMO position and optical absorption. In XAS data, the LUMO 0 and partial of LUMO+1 are electronically forbidden to transfer the conduction band of mesoporous TiO₂. The LUMO+2 and LUMO+3 states

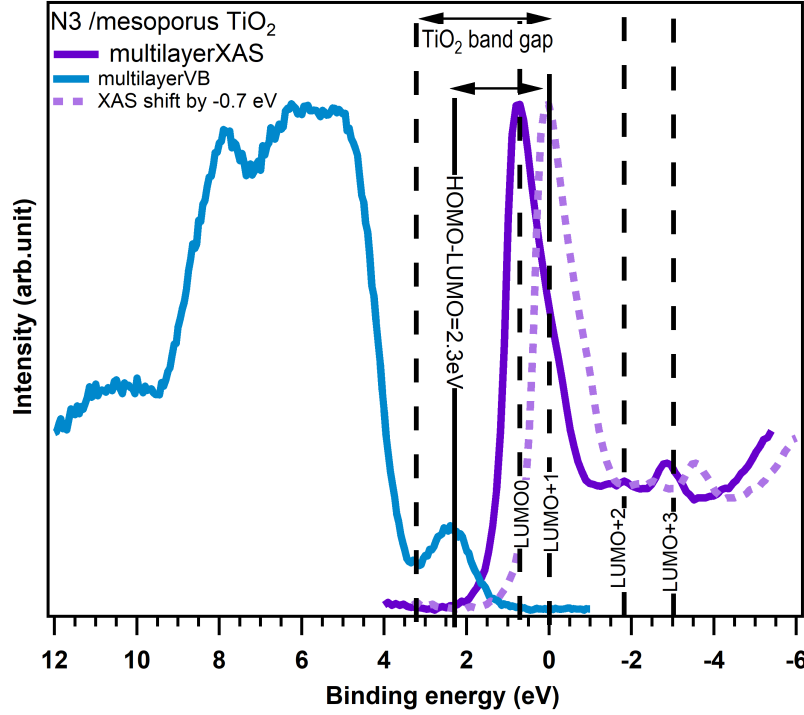


Figure 3.24: Combined valence-band photoemission and N K-edge NEXAFS spectra of multilayer N3 on mesoporous TiO₂. The purple solid represents the measured N K-edge X-ray absorption (NEXAFS) data, while the dashed purple line shows the corresponding energy-shifted spectrum used to align the optical HOMO–LUMO gap on a unified binding-energy scale. The blue line corresponds to the valence-band spectrum obtained by photoemission spectroscopy at a photon energy of 220 eV. Photoemission measurements were performed at normal emission, whereas the NEXAFS spectra were recorded in electron-yield mode.

overlap with the unoccupied level, facilitating electron transfer. The recently published valence band XPS of exposed mesoporous titania indicates a band gap of 3.1 ± 0.1 eV [30].

3.4 Resonant Photoemission Spectroscopy (RPES)

In DSCs, the initial reaction step involves electron injection from the excited molecule into the substrate’s conduction band. RPES has been used to examine charge transfer from molecules to substrates. This method allows for the quantification of charge delocalisation from unoccupied molecular orbitals to the substrate on a low femtosecond timescale, as previously demonstrated for the bi-isonicotinic acid ligand and the Ru 535 molecule on $\text{TiO}_2(110)$ [24, 85]. This technique is explained in detail in Chapter 2 section 2.2.3. Figure 3.23 shows that the LUMO of each N3 dye coverage facilitates charge transfer upon excitation with visible light.

As shown in Figure 3.25, the LUMO of the N3 dye, spatially localised on the bi-iso group, lies below the TiO_2 conduction band edge and does not participate in charge transfer in either monolayer or multilayer configurations. In contrast, higher orbitals such as the LUMO+1, which are mainly localised on the thiocyanate ligands, sit above the conduction band edge and can therefore participate in charge-transfer processes. While the LUMO in the band gap cannot transfer charge, it nevertheless serves as a reference for evaluating participant decay [86, 87].

Therefore, the interaction of the LUMO+3 orbital with the substrate is expected to be similar, as this orbital is energetically aligned with the TiO_2 conduction band, leading to comparable charge-transfer dynamics. The electron transfer dynamics are analysed using the core-hole clock implementation of RPES, in which charge transfer competes with the de-excitation of the excited state via resonant photoemission or resonant Auger processes. The duration of

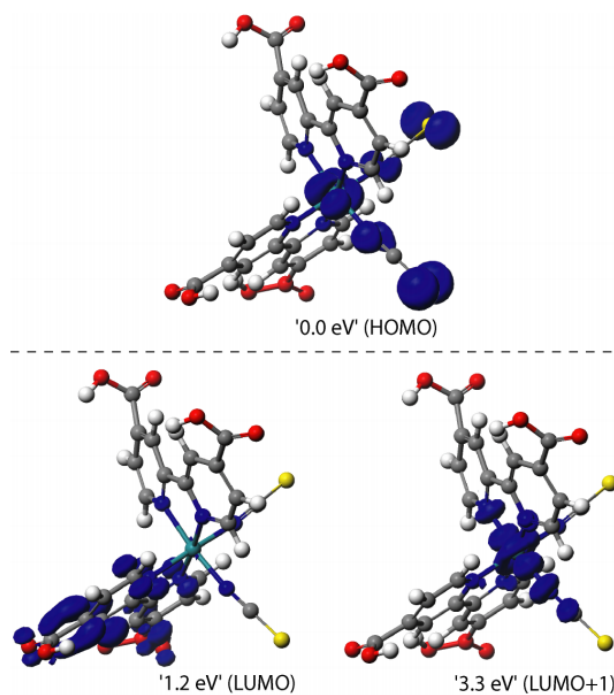


Figure 3.25: Calculated HOMO and LUMO orbital distributions of the N3 dye. The HOMO is mainly localised on the Ru centre, while the LUMO is spatially localised on the bi-isonicotinic ligand, consistent with its limited overlap with the TiO_2 conduction band. Adapted from Ref [24].

this de-excitation is characterised by the lifetime of the N 1s core hole. Within this framework, the electron injection time τ_{EI} is defined as the transfer of an electron from the LUMO+3 orbital of N3 into unoccupied states of the TiO₂ conduction band.

This study evaluates the electron injection time for N3 with varying TiO₂ nanoparticle coverages (thinnest, thin, and thick), where applicable. The injection time τ_{EI} is calculated according to Equation (3.1), with its derivation presented in Section 2.4.

$$\tau_{EI} = \tau_{CH} \cdot \frac{\frac{I(\text{mono}_{\text{RPES}})}{I(\text{mono}_{\text{NEXAFS}})}}{\frac{I(\text{multi}_{\text{RPES}})}{I(\text{multi}_{\text{NEXAFS}})} - \frac{I(\text{mono}_{\text{RPES}})}{I(\text{mono}_{\text{NEXAFS}})}} \quad (3.1)$$

The values $I(\text{mono}_{\text{RPES}})$ and $I(\text{multi}_{\text{RPES}})$ denote the intensities of the unoccupied peak under investigation in the monolayer and multilayer, respectively. These values are normalised by the total absorption cross sections (i.e., transition probability obtained from NEXAFS) calculated from the NEXAFS intensities $I(\text{mono}_{\text{NEXAFS}})$ and $I(\text{multi}_{\text{NEXAFS}})$. [88]. In the core-hole clock approach, τ_{CH} is treated as an approximately environment-independent reference value (6 fs for N₂) [88]. However, core-hole lifetimes can, in general, vary with the chemical environment, being longest for atomic Auger transitions and shorter for molecular transitions depending on the electronegativity of the ligands [89].

The upper limit of the core-hole lifetime is 7.5 fs for atomic nitrogen, as previously determined [89]. The experimental RPES data contain Auger peaks that must be excluded from the charge transfer analysis. The peaks are removed by integrating over a designated binding energy window, as illustrated in Figures 3.26 and 3.28 for both the multilayer and monolayer. Any peaks observed while sweeping the photon energy across the energies of the LUMO+2 and LUMO+3 resonances can be attributed exclusively to resonant photoemission, since normal photoemission only adds a sloping background. The LUMO+1 is excluded from consideration, as it cannot be distinguished from the LUMO

for these coverages. The RPES and NEXAFS spectra are normalised to the intensity of the LUMO; the resulting spectra are depicted in the left figures. In the NEXAFS spectra, the peaks indicate the complete intensities of unoccupied levels, while in RPES, the LUMO exhibits full intensity, but other unoccupied levels may be diminished due to charge transfer. In the multilayer, the LUMO+2 and LUMO+3 peaks are diminished in the RPES compared to the NEXAFS.

The intensity drop in the multilayer is only attributed to matrix element effects resulting from the various processes employed, as no charge transfer to the substrate can take place [82]. In the monolayer RPES, the peaks decreased further, in certain cases to the level of noise, signifying that charge transfer is occurring from these levels within the duration of the core-hole lifetime. Table 3.8 shows short summary RPES/NEXAFS ratios for thick and thin coverages of N3 dye molecules, together with the determined upper limit on the charge transfer timescale for the LUMO+3 orbital examined.

3.4.1 N3/TiO₂ nanoparticles

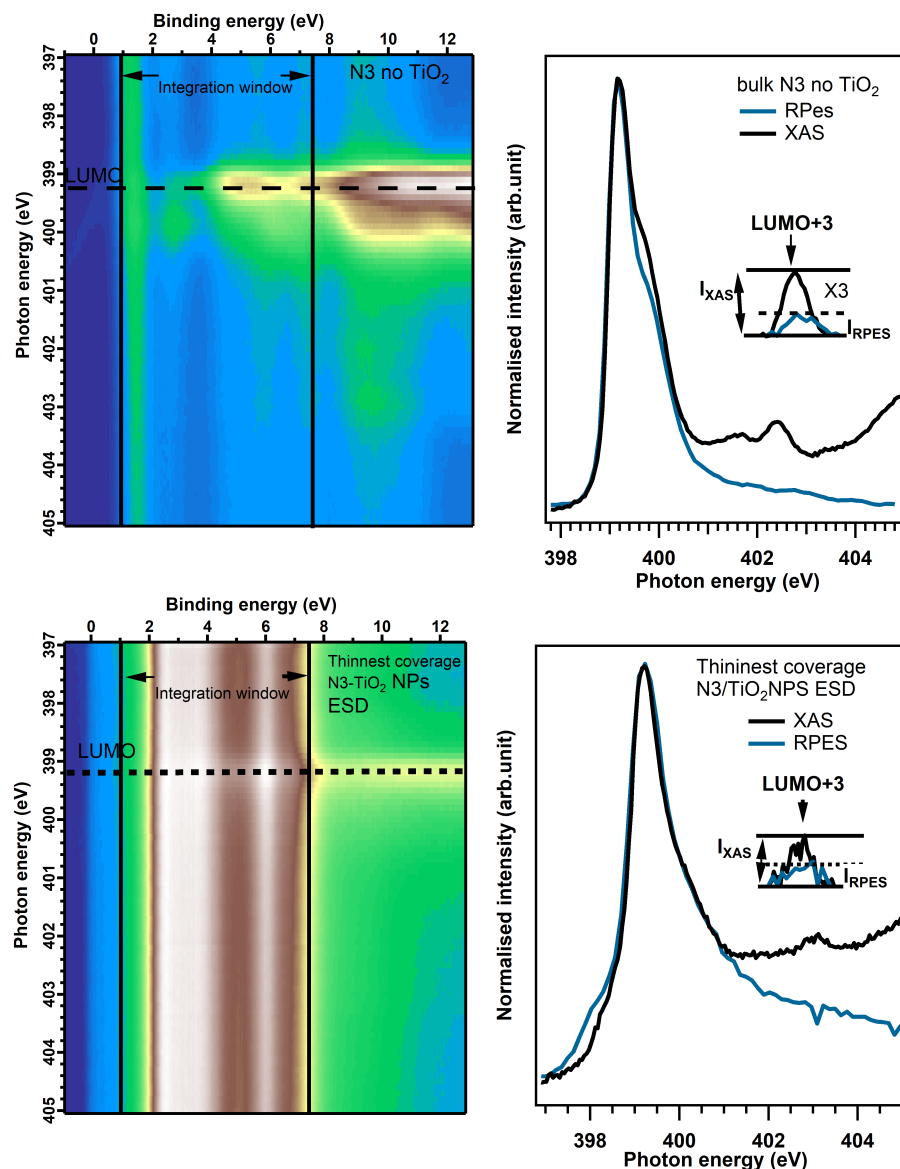


Figure 3.26: N 1s RPES of bulk N3 without TiO₂. The figure beside it acts XAS & RPES at integration window (1–7.5 eV). The bottom map is RPES of the thinnest N3 film on TiO₂ NPs by ESD, and the figure beside it is the XAS & RPES at integration window (1–7.5 eV).

Figure 3.26 shows the resonance map of bulk N3 on Au(111) measured with the thinnest coverage of N3 on TiO₂ NPs. The charge-transfer duration from LUMO+3 to the substrate's conduction band is determined using the core-hole clock implementation.

The computed relative intensities of the participatory channel in the RPES, expressed as a proportion of the total X-ray absorption for LUMO+3, is $I(\text{mono})_{\text{RPES}}/I(\text{mono})_{\text{NEXAFS}} = 0.10.02$. At the same time, the equivalent value for bulk N3 is $I(\text{multi})_{\text{RPES}}/I(\text{multi})_{\text{NEXAFS}} = 0.30.02$. The charge transfer duration from LUMO+3 to the conduction band of TiO_2 NPs is determined to be 30.02 fs. It is expected because the thinnest coverage corresponds to a permanent TiO_2 layer on Au, the electron in the LUMO+3 of N3 is expected to transfer rapidly to the TiO_2 conduction band, as indicated by the extracted timescale of 0.1 0.02 fs.

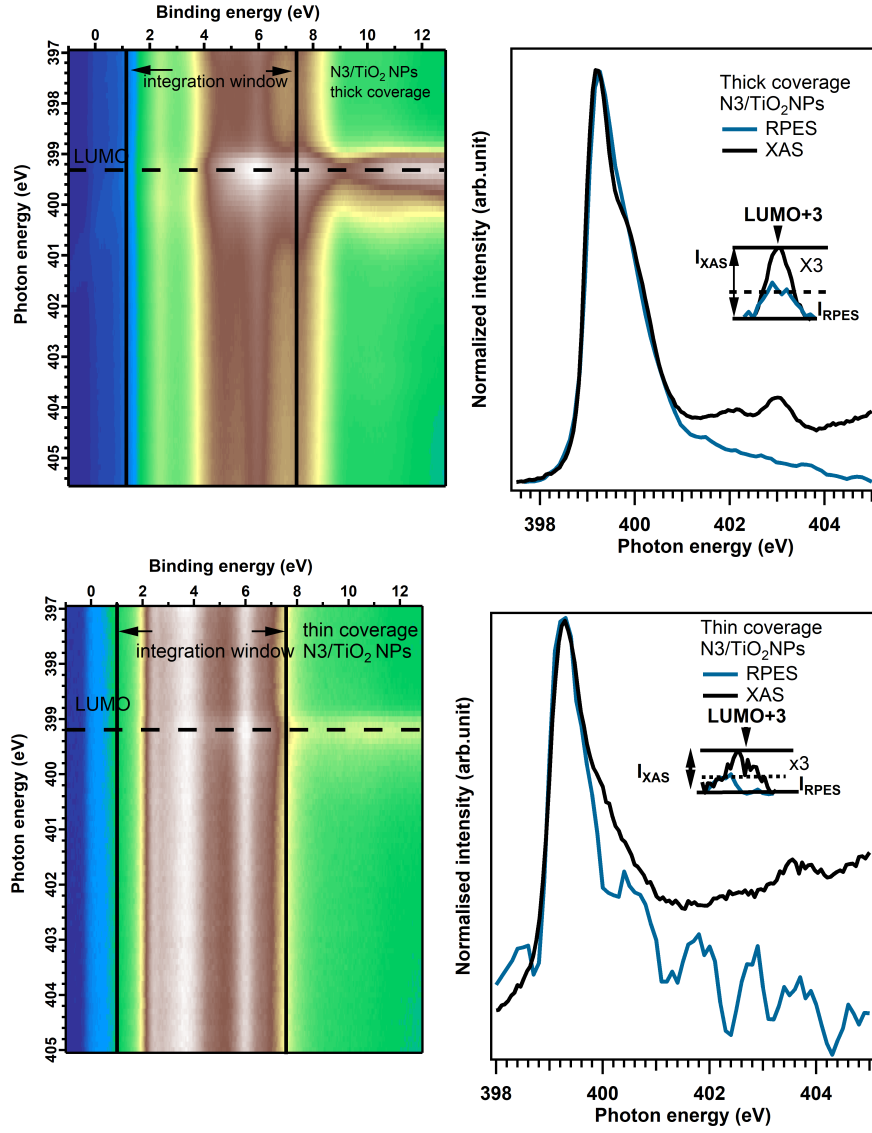


Figure 3.27: the RPES of thick N3 coverage on TiO_2 NPs. The figure beside it shows the corresponding XAS and RPES spectra within the integration window (1 – 7.5 eV). The bottom map is RPES of thin N3 on TiO_2 NPs and the fig beside it is t XAS & RPES at integration window (1 – 7.5 eV).

Figure 3.27 shows the resonance map of a thick coverage of N3 on TiO_2 NPs, compared to the thin coverage of N3 on TiO_2 NPs. The charge-transfer duration from LUMO+3 to the substrate’s conduction band is determined using the core-hole clock implementation. The calculated relative intensities of the participatory channel in the RPES, expressed as a proportion of the total X-ray absorption for LUMO+3, is $I_{\text{RPES}}^{(\text{mono})}/I_{\text{NEXAFS}}^{(\text{mono})} = 0.20.02$. At the same time, the equivalent value for thick N3 is $I_{\text{RPES}}^{(\text{multi})}/I_{\text{NEXAFS}}^{(\text{multi})} = 0.30.02$. The

charge transfer duration from LUMO+3 to the conduction band of TiO_2 NPs is determined to be 10.90.02 fs. This agrees with the upper time limit for electron injection of N3 on TiO_2 at LUMO+3, previously determined to be approximately 12 fs [63].

3.4.2 N3 on mesoporous TiO_2

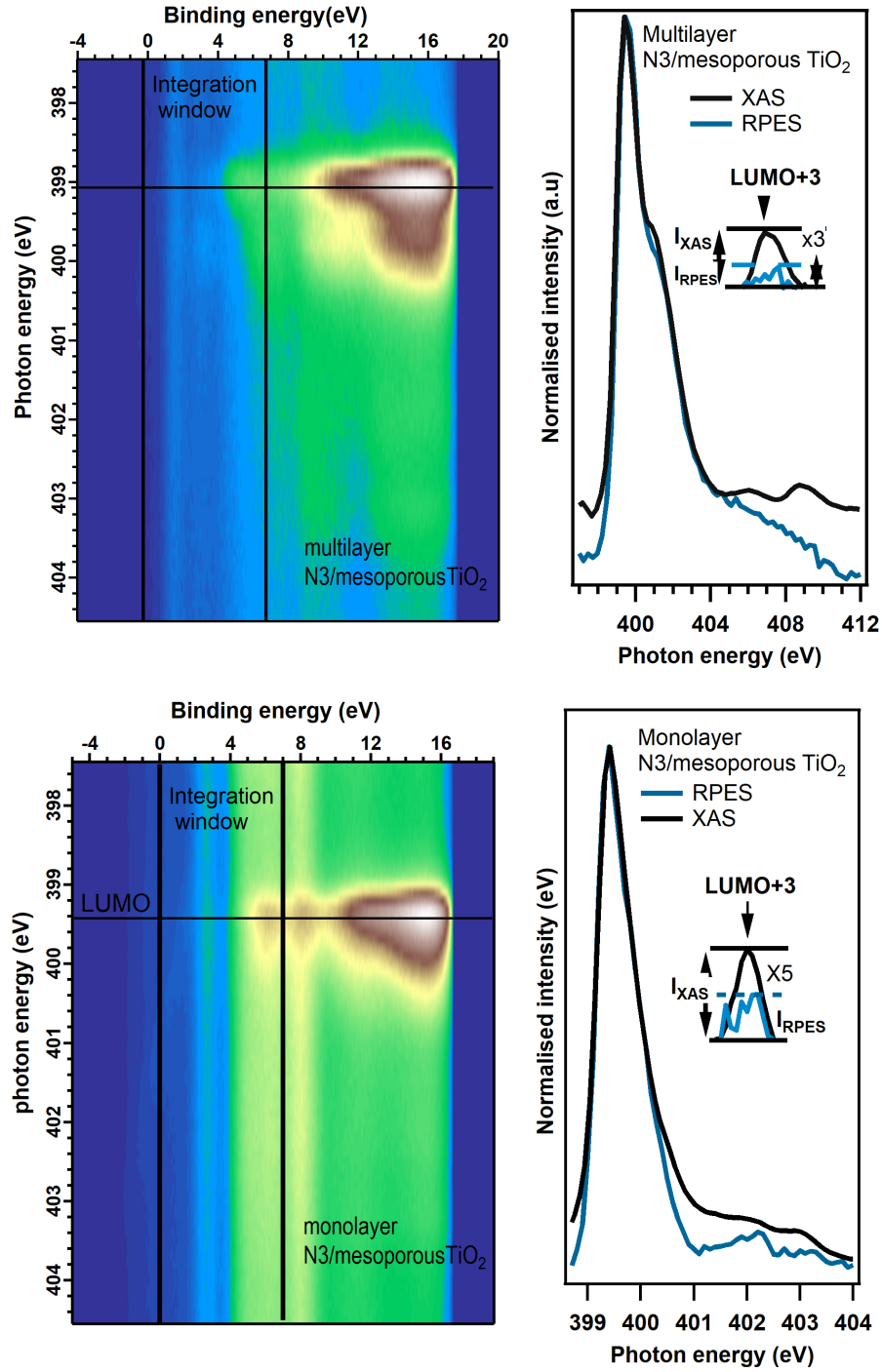


Figure 3.28: Top panels show the RPES maps of multilayer N3 on mesoporous TiO_2 . The adjacent panels display the corresponding XAS and RPES spectra extracted within the integration window (1 – 7.5 eV). The bottom panels present the RPES maps of monolayer N3 together with the associated XAS and RPES spectra obtained from the same integration window.

Figure 3.28 shows the resonance map of a multilayer of N3 on mesoporous TiO₂, compared with the monolayer of N3 on mesoporous TiO₂. The charge-transfer duration from LUMO+3 to the substrate’s conduction band is calculated using the core-hole clock implementation. The computed relative intensities of the participatory channel in the RPES, expressed as a proportion of the total X-ray absorption for LUMO+3, are $I_{\text{RPES}}^{(\text{mono})}/I_{\text{NEXAFS}}^{(\text{mono})} = 0.50.02$. At the same time, the equivalent value for multilayer N3 is $I_{\text{RPES}}^{(\text{multi})}/I_{\text{NEXAFS}}^{(\text{multi})} = 0.660.02$. The charge transfer duration from LUMO+3 to the conduction band of mesoporous TiO₂ is determined to be 18.70.02 fs. This agrees with the upper time limit for electron injection of N3 on TiO₂(110), previously determined to be approximately 16 fs [24].

Table 3.8: RPES / NEXAFS ratios for different coverages of N3 dye molecules. Here, ‘bulk N3’ refers to a sample consisting of a thick film of N3 deposited without TiO₂; in this case, there is no charge transfer, and the timescale is considered infinite. ‘Thick coverage’ is defined as multiple continuous molecular layers (more than one monolayer) of N3 deposited on TiO₂ such that several layers are present but still permit finite charge transfer due to interfacial contact with TiO₂. The extracted upper limits on the charge-transfer timescale for the LUMO+3 orbital are also provided.

Coverage	Thick	Thin	Upper limit on charge transfer timescale
	RPES / NEXAFS	RPES / NEXAFS	(fs)
Thinnest / Bulk	0.3±0.02	0.1±0.02	3±0.02
Thin / Thick	0.3±0.02	0.2±0.02	10.9±0.02
Monolayer / Multilayer	0.6±0.02	0.5±0.02	18.7±0.02

3.5 Summary and Conclusions

N3 dye was deposited onto TiO₂(110) using an electrospray deposition system operating under ultra-high vacuum (UHV). Additional samples with varying

N3 thicknesses were prepared, including thinnest layers produced by electro-spray deposition (ESD) and thin, medium, thick, and bulk films formed on Au(111) by drop casting, together with mesoporous TiO₂ substrates. They have been investigated by X-ray photoemission, resonant photoemission, and X-ray absorption spectroscopy. The XPS results indicate that N3 bonds to TiO₂(110), mesoporous TiO₂, and TiO₂ NPs via the deprotonation of carboxylic acid groups.

Hydrogen atoms in the carboxylic group also contribute to the oxygen bridge on the titanium surface. The sulphur atoms in the thiocyanate group, which show variety bonds, could bond to O_{lattice} on the Ti surface, Au(111), and Ti. The N 1s NEXAFS indicates that the LUMO and partial LUMO+1 are entirely located within the band gap of mesoporous TiO₂ and TiO₂ NPs, respectively. This leads to an electronic forbiddenness of electron transfer between the LUMO, the partial LUMO+1, and the substrates. The LUMO+2 and LUMO+3 states of the excited core molecules overlap with the unoccupied states in the substrate. The decreased intensity in the participant channel of the LUMO+2 and LUMO+3 states observed in RPES indicates that charges rapidly transfer to the surface during the core-hole lifetime.

Comparing the relative intensities of the participant channel to the NEXAFS for bulk N3 separated with the thinnest coverage of N3 on TiO₂ NPs, thin and thick coverage of N3 on TiO₂ NPs, and monolayer and multilayer of N3 on mesoporous TiO₂ simplified our understanding of charge transfer over time. The charge-transfer time from the LUMO+3 orbital to the conduction band was calculated as 3 ± 0.02 fs for the thinnest N3 coverage on TiO₂ nanoparticles, 10.9 ± 0.02 fs for thick N3 coverage on TiO₂ nanoparticles, and 18.7 ± 0.02 fs for monolayer and multilayer N3 on TiO₂ mesoporous.

Chapter 4

XPS and RPES Study of the Electronic Structure of D5 Adsorbed on TiO₂ Surfaces

4.1 Introduction

Nanostructured dye-sensitised solar cells (DSSCs) provide promising alternatives to traditional silicon-based solar cells [12]. Metal-organic complexes have long led the way in photo-conversion efficiency [12, 23, 90–94]. Exciting progress now centres on metal-free organic dyes, valued for their high extinction coefficients and adaptable structures. Among these, diphenylamine-based dyes—especially the polyene-diphenylaniline dye (D5) [21] are turning heads with strong performance [21, 95]. In D5, the diphenylamine group donates electrons, while the cyanoacetic group pulls electrons in and anchors the molecule to TiO_2 , as shown in Figure 4.1.

As discussed in Chapter 3, efficient photocurrent generation depends on strong chemical coupling between the dye and TiO_2 . Similarly, energy coupling is crucial for fast electron injection into the TiO_2 conduction band [96–98]. Although the operation of the N3 dye system is well understood, the complex interfacial electronic structure and charge-transfer operation of D5 remain incompletely explained.

The experiments in this chapter address these questions. Using X-ray photoelectron spectroscopy (XPS), density of states (DoS), and resonant photoemission spectroscopy (RPES), we examine how D5 interacts with several titanium dioxide TiO_2 surfaces. We compare its molecular anchoring and electronic alignment to those of the N3 dye. This analysis clarifies whether organic dyes like D5 can match or exceed the coupling mechanisms seen with N3. It also advances our understanding of dye-semiconductor interactions in dye-sensitised solar cells (DSSCs).

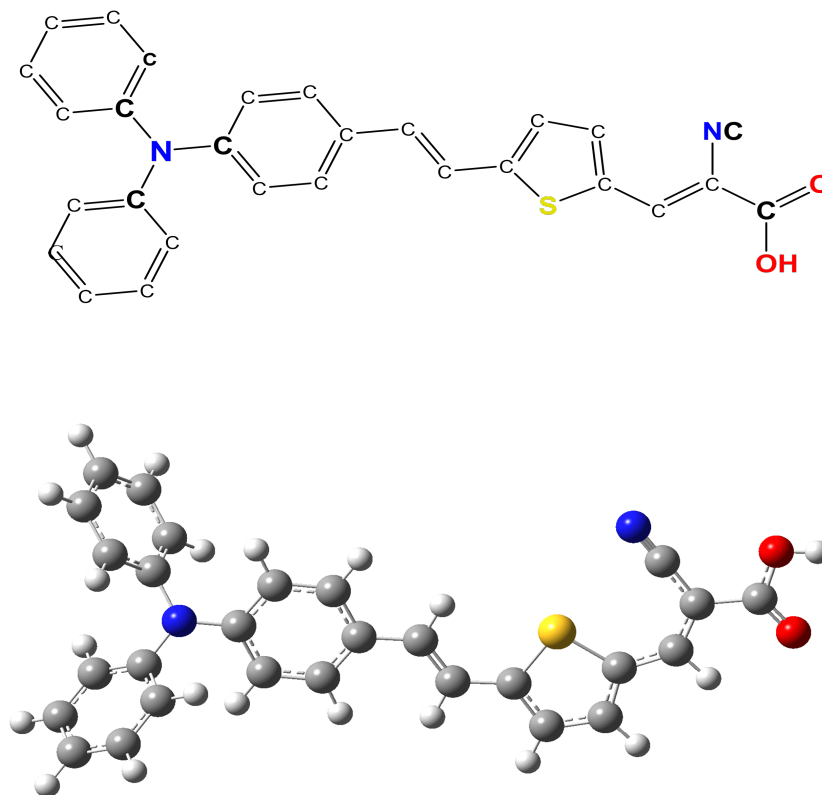


Figure 4.1: Structure of the D5 molecule.

4.2 D5 on single rutile $\text{TiO}_2(110)$

4.2.1 Methods

The preparation and deposition of rutile $\text{TiO}_2(110)$ substrate involved cleaning the substrate multiple times, annealing at 600°C , and scanning the XPS spectra until the C 1s peak disappeared. The D5 solution was prepared early and applied to the substrate under laser irradiation. The electrospray system was isolated from the preparation chamber using an ultra-high vacuum gate valve. The pressure within the chamber increased during electrospray, possibly because solvent molecules were not entirely removed. The deposition coverage changes over time, with measurements taken after each deposition. It is the same method that we have used in the first section 3.2. The XPS results were calibrated to the Ti $2p_{3/2}$ substrate peak, recorded at 458.8 eV [69]. The Shirley and linear backgrounds were removed from the spectra, and a pseudo-Voigt function, a combination of Gaussian and Lorentzian profiles, was used

for curve fitting. The dataset utilised in this study followed a fitting process that included a 30% Lorentzian distribution and a 70% Gaussian distribution. This method approximates a Voigt profile.

4.2.2 Results and Discussion

Figure 4.2 shows the O 1s XPS spectrum. The left panel is the deposition by ESD over different times (20, 40, and 60 mins), and the right panel is the deposition when the ion gate is on over time, 20 mins and 40 mins. The O 1s spectra were analysed using same method to analyse the O 1s data has four environment peaks: Ti–O (TiO_2), C=O/ COO^- , Ti–OH, and C–OH. The deposition by ESD from 20 minutes to 60 minutes, at the peak of 530 eV, comes from the $\text{TiO}_2(110)$ substrate; it is most noticeable at 20 minutes of deposition, and the intensity of the peak decreases at 40 minutes and 60 minutes. This is expected because the D5 layer thickens over time. At a 20-minute deposition, the peak at 531.3 eV is assigned to the hydrogen atom in carboxyl bonded to the oxygen bridge Ti substrate, which agrees with Zhang et al study [70]. A single molecule peak appears at 532.3 eV, which is attributed to COO^- . This energy value is ascribed to the deprotonation of the carboxylic acid group and the deprotonation of the oxygen atoms to titanium atoms on the oxide surface. Adsorption mechanism to the surface has been found before for the molecule of 2-Cyano-3-(4-N, N-diphenylaminophenyl)-trans-acrylic acid when it is heated and placed onto rutile $\text{TiO}_2(110)$ [99], which is a special characteristic of carboxylic acids on titanium dioxide [24, 63]. It has definitely matched the previous chapter TiO_2 3 is N3 on TiO_2 in Section 3.2. The final peak in the O 1s spectrum at 20 minutes of deposition, which is at 533.6 eV, is linked to C–OH, with the ratio of the peaks C=O/ COO^- , Ti–OH, and C–OH being 2:1:1. This indicates the molecular arrival of the $\text{TiO}_2(110)$ substrate. As the coverage increases to 40 min and 60 min, the peak at 530 eV, assigned to TiO_2 , decreases, as expected, because the layer becomes thicker over time and the

TiO_2 signal decreases.

This differs from [22], where the O 1s signal from the COO^- group was reported to show no significant variation within the studied time range. By contrast, in this study, the O 1s intensity increases with deposition time, showing progressive growth in D5 coverage on the TiO_2 surface. While the intensities of two additional peaks, C=O and C–OH, increased until they reached a 1:1 ratio, this occurred for the carboxyl group in thick coverage, which did not undergo deprotonation. The right panel of Figure 4.2 displays the O 1s XPS spectrum at two time points: 20 minutes and 40 minutes, while the ion gate is activated. At 20 minutes, the spectrum resembles the O 1s spectrum obtained by ESD, rather than showing a peak intensity ratio of C=O/ COO^- , Ti–OH, and C–OH of 2:1:0.5. At 40 minutes, the spectrum matches the O 1s spectrum observed at 20 minutes by ESD. This indicates that using the ion gate reduced surface molecule density, likely by filtering ions from the beam, leaving fewer molecules to deposit. Still, XPS confirms D5 molecules are present in both cases, which is the central result.

Figure 4.3 displays the N 1s XPS spectra, which are fitted with three and two components, for all coverages at different time intervals of 20, 40, and 60 minutes during ESD deposition. The right panel displays the N 1s spectrum at 20 and 40 minutes when the ion gate is activated. Two peaks are present in the molecular spectrum, with one identified as contamination (part of the holder for the substrate), specifically Mo $3p_{3/2}$ at 396.3 eV. These peaks correspond to nitrogen atoms in triphenylamine (C–N) at 400 eV and nitrile ($\text{C}\equiv\text{N}$) at about 399 eV. Earlier XPS analyses of the identical moieties of diphenylamine and nitrile in L0 and D5 corroborate these assignments [22, 30]. The ratio of the two N 1s components is about 5.1:1, 8.2:1, and 44.7:1 at 20 minutes, 40 minutes, and 60 minutes, respectively. The intensity of TPA increases over time, while the nitrile signal decreases, which is consistent with the nitrile group being located at the molecular bottom.

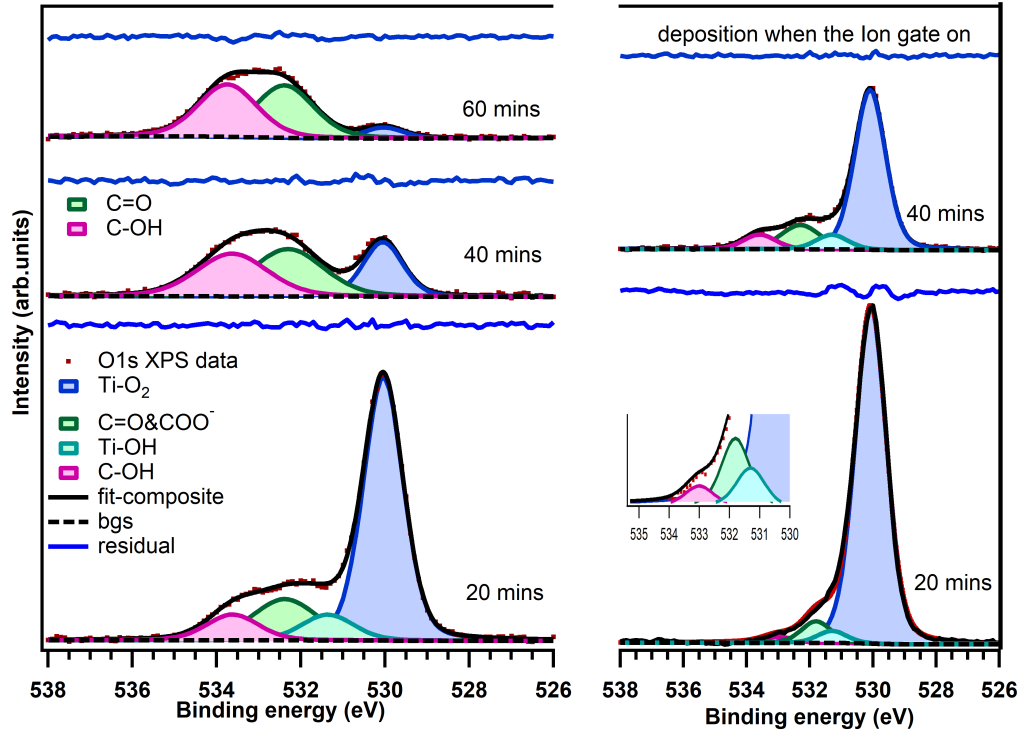


Figure 4.2: High-resolution spectra O 1s XPS spectra of TiO_2 surfaces during deposition at different time intervals (20, 40, and 60 minutes) with ESD (left) and when the ion gate is on (right). The black line indicates the comprehensive fitted spectrum, whereas the blue line in the upper section of each panel illustrates the residuals of the fit.

As the layer thickness increases, XPS can no longer detect the nitrile-related N 1s component, supporting the observations in the O 1s data (Figure 4.2). While the N 1s intensity increased when the ion gate was on, the Mo 3p_{3/2} peak intensity decreased over the course of deposition, being weaker at 40 minutes compared to 20 minutes. The ratio of TPA to nitrile is 13.5:1 at 40 minutes and 2:1 at 20 minutes. This matches prior findings for D5, where the (C≡N) intensity decreases at longer deposition times, possibly due to shadowing of that end of the molecule caused by carboxylic acid anchoring to the surface, as indicated by the O 1s data [22, 30]. Variations in the N 1s intensity provide insight into molecular arrangement during deposition, even when the overall coverage remains close to a monolayer.

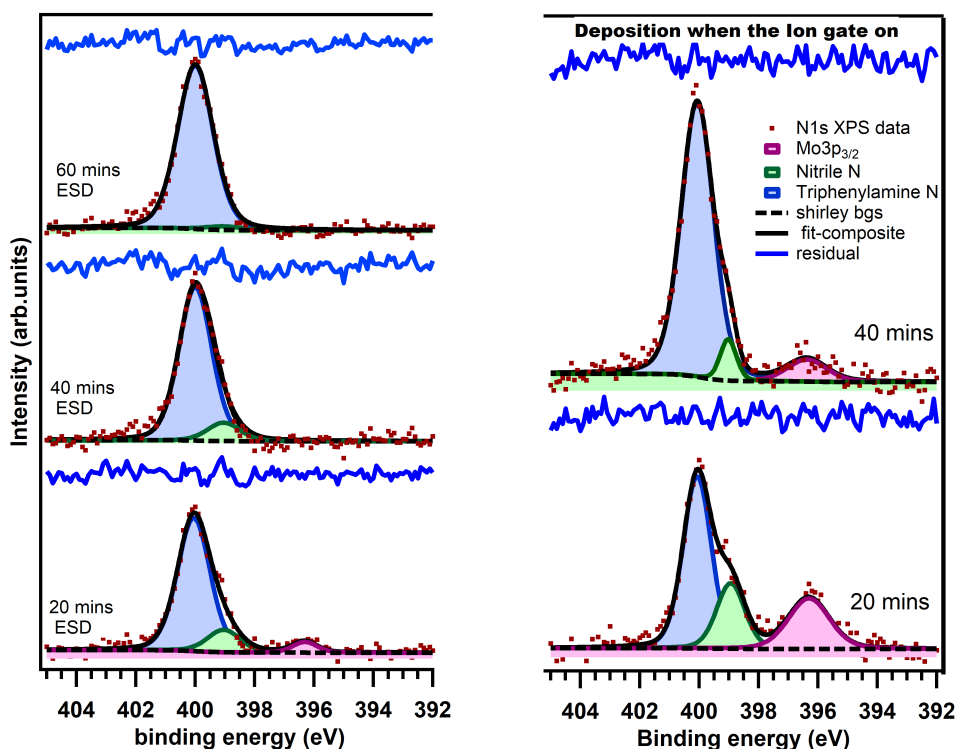


Figure 4.3: High-resolution images N 1s XPS spectra of $\text{TiO}_2(110)$ surfaces during deposition at different time intervals (20, 40, and 60 minutes) with ESD (left) and when the ion gate is on (right). The black line indicates the comprehensive fitted spectrum, whereas the blue line in the upper section of each panel illustrates the residuals of the fit.

Figure 4.4 presents the corresponding C 1s XPS for D5. The left panel shows the spectra for D5 deposited by ESD over different times (20, 40, and 60 min), whereas the right panel shows the C 1s XPS when the ion gate is open. All BE (eV) for peaks, and their ratios are listed in Table 4.1. The spectrum can be fitted to three components in the main peak and an additional peak to higher binding energy. The high-binding-energy component assigned to the deprotonated carboxylate group appears at 289.5 eV. Only this component is shifted relative to previous reports, while the other C 1s components remain at their expected binding energies. This is in disagreement with previous publications; they found this peak at 288.7 eV in this study is a little bit higher in all coverage. The main contribution of the component at 285.3 eV, attributed to the aromatic ring, arises from the C 1s carbon atoms in the phenyl rings of the triphenylamine group and the molecular backbone. The peak at 286 eV is associated with carbon atoms bonded to nitrogen in the triphenylamine and cyano group, while the peak at 287.0 eV corresponds to the thiophene group.k.

In the molecule, the components in the above order have a 21:4:2:1 ratio, which compares well to the 20:4:2:1 intensity ratio observed in Figure 4.4. The COO^- component was constrained during fitting to reflect the expected stoichiometric ratio of the molecule. For the simple L0 molecule [30], Temperton. et al observed shake-up features at higher energy levels ranging from 290 to 292 eV. In this study, we observe no clear evidence of shake-up features here. This agrees with a recent study of D5 on $\text{TiO}_2(110)$ [22].

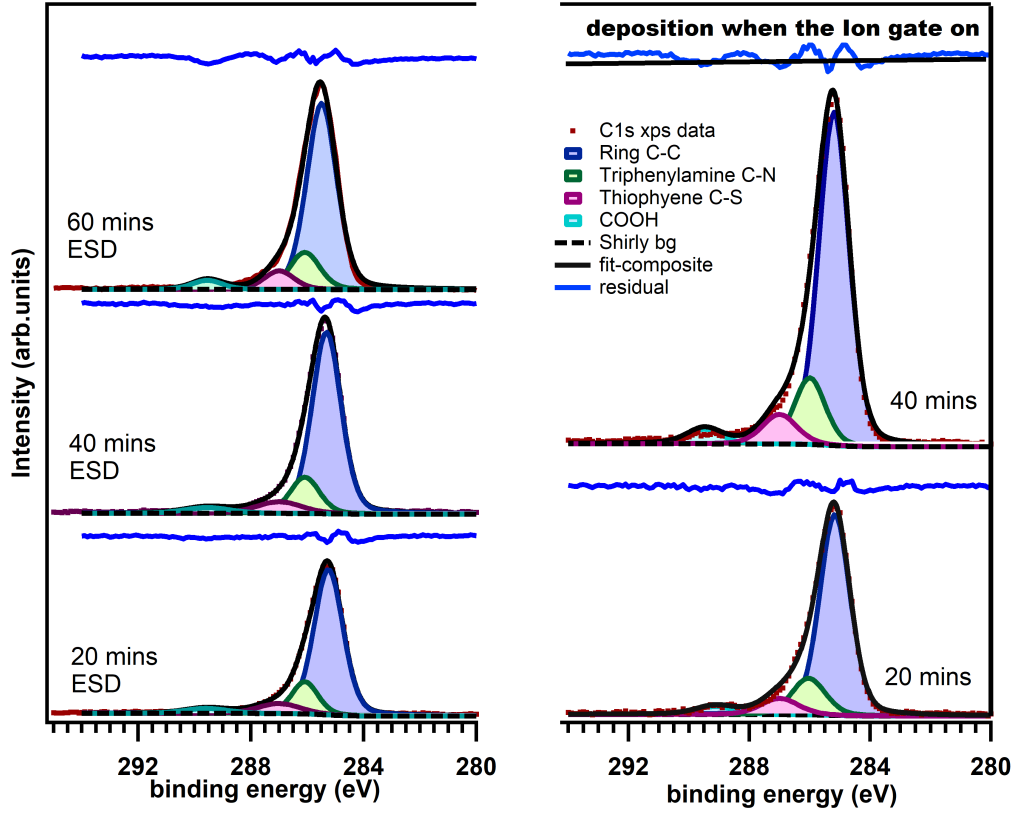


Figure 4.4: High-resolution images C 1s XPS spectra of $\text{TiO}_2(110)$ surfaces during deposition at different time intervals (20, 40, and 60 minutes) with ESD (left) and when the ion gate is on (right). The black line indicates the comprehensive fitted spectrum, whereas the blue line in the upper section of each panel illustrates the residuals of the fit.

Table 4.1: A summary of the XPS component binding energies for C 1s of D5 on $\text{TiO}_2(110)$ surface by ESD and when the Ion gate is on.

peak	ESD		When the ion gate is on	
	20, 40, 60 min	area	20, 40 min	area
Ring C–C	285.2	20	285.2	20
Triphenylamine N	286	4	286	4
Thiophene	287	2	287	2
COOH	289,5	1	289.1	1

The S 2p XPS spectra are shown in Figure 4.5 for samples deposited by ESD, with the bottom spectrum representing a deposition time of 60 minutes and the top spectrum corresponding to when the ion gate is on at 40 minutes, revealing

closely spaced peaks around 1.2 eV with a ratio of 2:1. The S $2p_{3/2}$ binding energies have been measured at 164.3 eV and 164.6 eV, respectively. The result is that the thiophene does not interact with $\text{TiO}_2(110)$, as is consistent with earlier studies [22, 100].

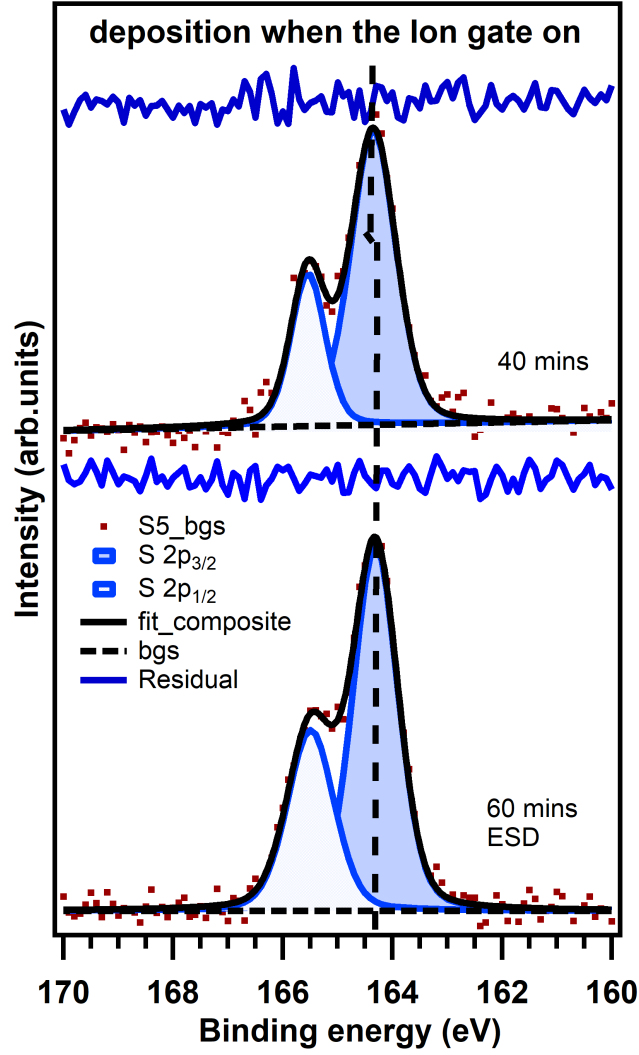


Figure 4.5: High-resolution S 2p XPS spectra acquired after 40 minutes (top) with the ion gate activated and 60 minutes (bottom) of deposition with ESD.

4.3 D5 on mesoporous TiO₂

4.3.1 Methods

Sample Preparation

Mesoporous TiO₂ on FTO glass (Solaronix) was soaked in an ethanol-dissolved D5 solution for 12 hours in a nitrogen atmosphere to produce monolayer samples. The treated electrodes were cleaned and soaked in ethanol again to remove any dye that had physisorbed. On Si/SiO₂ surfaces that were heated to about 200°C, multiple layers of D5 were formed by electrospray deposition (ESD) in vacuum, as described in Section 2.5.1. This procedure was conducted using an Al K α X-ray source (1486.6 eV) and a Phoibos 150 hemispherical analyser in a SPECS DeviSim NAP-XPS system [101].

Beamline

XPS measurements were carried out at the I09 beamline of Diamond Light Source in the United Kingdom. Both soft and hard X-ray beams are available from the beamline; the former is used for measurements using photoelectron spectroscopy (PES). The beam was defocused to $400 \times 400 \text{ }\mu\text{m}^2$ in order to reduce average changes and damage from the mesoporous substrate. To reduce beam damage, the undulators were detuned and defocused by a factor of $\times 20$ for the soft beam and $\times 40$ for the hard beam. With a resolving power of $\times 10,000$, the beamline provides resolutions of approximately 0.25 eV and 0.28 eV at the S 1s level. Measurements were taken at an angle of 10° from the straight line of emission (80° from the beam direction) using a VG Scienta EW4000 analyser, which can accept angles of 56° on the beamline [101].

X-ray Photoelectron Spectroscopy (XPS)

We conducted XPS using a photon energy of 2.7 keV to enable hard X-ray photoelectron spectroscopy (HAXPES) measurements with improved sensitivity to buried interfaces. and a pass energy of 100 eV in swept mode. All the binding energy scales were calibrated to the Ti 2p_{3/2} peak at 458.8 eV.

4.3.2 Results and discussion

Hard X-ray Photoelectron Spectroscopy

Figure 4.6 shows the O 1s HAXPS spectrum of D5 on mesoporous TiO_2 ; the bottom figure acts as a monolayer, and the top figure is a multilayer. Table 4.2 lists all the BEs. In both coverages, the peak at 530 eV is assigned to TiO_2 . The O 1s signal observed here is much stronger than in previous monolayer and multilayer measurements. This increase results from the higher photon energy used in these HAXPES experiments, which allows for greater electron escape depth. As a result, more oxide oxygen atoms contribute to the spectrum compared to the more surface-sensitive soft X-ray measurements. The second peak at 531.4 eV corresponds to COO^- , which is commonly associated with the deprotonation of the COOH group [22, 24, 30, 63]. The third peak, located at 531.3 eV, is assigned to the H atom, which is bonded to the O bridge of the Ti surface [70].

The last peak is C–OH, positioned at 532.4 eV for monolayer and 532.6 eV for multilayer. In the monolayer, the peak at high binding energy (536.1 eV) is a shake-up feature, generated by an electronic transition during photoemission. In multilayer, we accepted that the C=O and C–OH will increase their intensity to be 1:1; however, in this study, the spectrum of the monolayer is similar to that of the multilayer. The main result is that the COOH group gets deprotonated and bonded to the mesoporous TiO_2 surface.

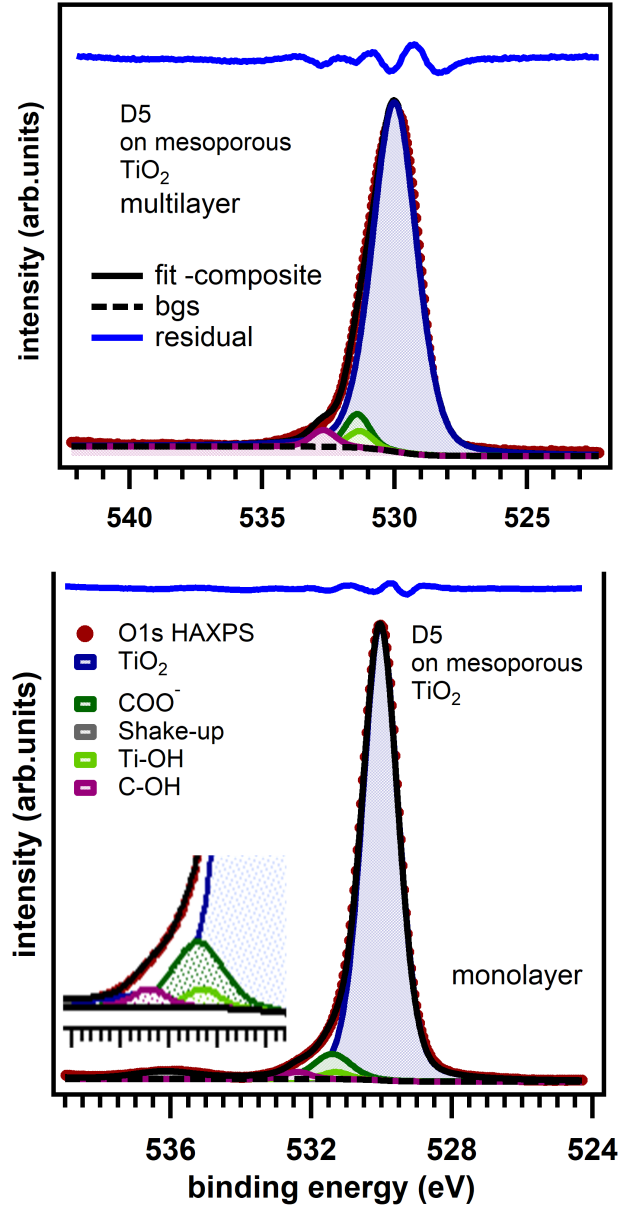


Figure 4.6: O 1s HAXPS spectrum of D5 on mesoporous TiO_2 , Lower spectrum: monolayer, upper spectrum: multilayer.

Table 4.2: A summary of the HAXPS component binding energies for O 1s of D5 on mesoporous TiO_2 surface.

peak	monolayer	multilayer
TiO_2	530	530
COO^-	531.4	531.4
Ti-OH	531.3	531.3
C-OH	532.4	532.6

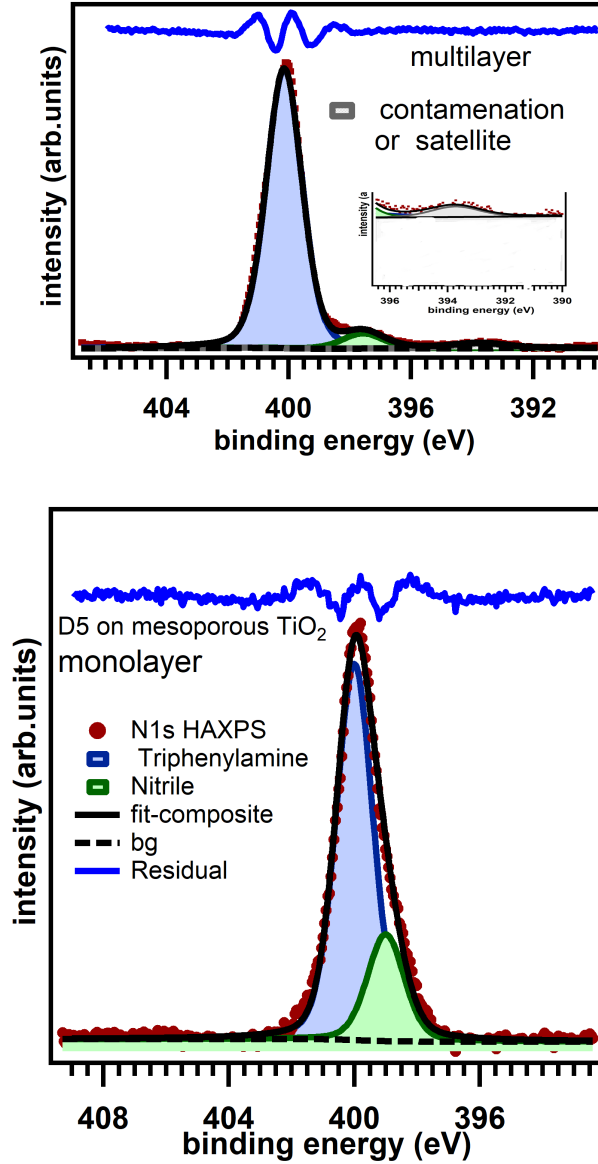


Figure 4.7: N 1s HAXPS of D5 on mesoporous TiO_2 , Lower spectrum: monolayer, upper spectrum: multilayer. The blue curve shows the residuals (data - fit); the vertical scale indicates the deviation relative to the signal intensity.

Figure 4.7 shows the N 1s HAXPS spectrum of D5 on mesoporous TiO_2 ; the bottom figure acts as a monolayer, and the top figure is a multilayer. Table 4.3 lists all the BEs. Temperton et al. identified two peaks: one for the nitrile $\text{N}\equiv\text{C}$ and another for triphenylamine $\text{N}-\text{C}$ in the accepted monolayer; the nitrile peak is located at 399 eV [30]; however, in the multilayer, it shifts to 397.6 eV, suggesting a lower binding energy that could arise from a change in the nitrile group's chemical environment. The peak may shift to a lower

binding energy because molecules in a multilayer may interact differently with the surface or with one another than in a monolayer. This could change the electron density surrounding the nitrogen atom. The second peak, which corresponds to triphenylamine N–C, is found at the same binding energy of 400 eV for both coverage levels, consistent with the literature and the previous study discussed in section 4.2.2. In the multilayer, an extra peak at 397.6 eV could be due to satellite peaks or contamination. The ratio between the nitrile N≡C peak and the triphenylamine N–C peak would be expected to approach 1:1; however, the measured N 1s spectrum of D5 does not show an exact 1:1 intensity ratio.

This discrepancy is primarily due to molecular orientation and the technique’s surface sensitivity. The dye tends to orient upright when anchored to the TiO₂ surface via its carboxylic acid group. This causes the nitrile nitrogen to penetrate deeper into the molecular layer, while the triphenylamine nitrogen remains closer to the surface. XPS is very surface-sensitive, so it picks up signals from surface atoms more strongly and attenuates signals from deeper layers.

Because of this, the signal from the nitrile nitrogen is weaker, and the intensity ratio is about 3:1 in favour of the triphenylamine nitrogen. Previous studies utilising XPS [22, 43] have confirmed the validity of this depth effect. Variations in bonding configurations or the presence of residual molecules on the surface can influence the observed ratio. This provides a good insight into the orientation and interaction between D5 and mesoporous TiO₂. A previous study [30] on the L0 molecule on mesoporous TiO₂ confirmed this result.

Table 4.3: A summary of the HAXPS component binding energies for N 1s of D5 on mesoporous TiO₂ surface.

peak	monolayer	multilayer
Nitrile N $\equiv$ C	399	397.6
Triphenylamine N–C	400	400

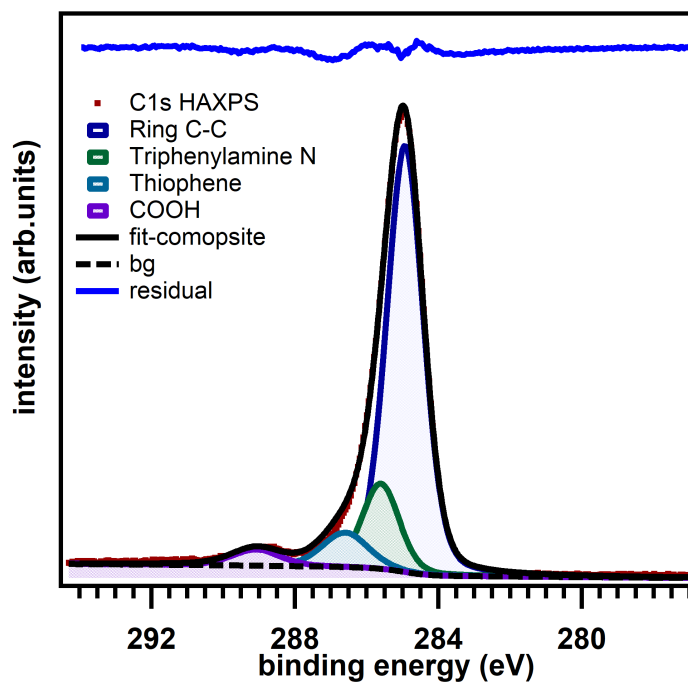
**Figure 4.8:** N 1s HAXPS of D5 on mesoporous TiO₂, the bottom is monolayer and the top is multilayer.

Figure 4.8 shows the C 1s HAXPS spectrum of D5 on mesoporous TiO₂. Table 4.4 lists all the binding energies. This figure represents the best fit for C 1s, where the small peak at 289 eV has its intensity fixed to align with the other peaks; it is assigned to COOH. The dominant peak at 284.9 eV corresponds to the ring C–C and the backbone of the molecule. The subsequent peak at 285.6 eV is attributed to the carbon atoms bonded to nitrogen in the triphenylamine and cyano groups, while the peak that is shifted by 1 eV corresponds to a thiophene carbon atom bonded to sulphur. The intensity ratio of these peaks is 20:4:2:1, compared to the stoichiometric ratio within the molecule of 22:4:2:1 for ring C–C: triphenylamine: thiophene: COOH. There is a slight decrease

in the intensity of the ring C–C in comparison to the original ratio of 22:4:2:1. This observation aligns with a study by Nouf [22]. No shake-up was observed at 290 – 292 eV, as reported in the study by L0 [30], despite the photoemission window exceeding 294 eV.

Table 4.4: A summary of the HAXPS component binding energies for C 1s of D5 on mesoporous TiO₂ surface.

peak	BE (eV)
Ring C–C	284.9
Triphenylamine C–N	285.6
Thiophene C–S	286.6
COOH	289

4.4 D5 on TiO₂ NPs

4.4.1 Methods

The preparation was conducted in our laboratory at the University of Nottingham by combining TiO₂ nanoparticles (21 nm) with the D5 dye complex, sourced from Sigma-Aldrich and Merck. The TiO₂ solution concentration was 0.1 wt% (0.015 g of TiO₂ and 15 g of ethanol). A small quantity of D5 dye particles was incorporated into 0.1 wt% TiO₂, and it underwent five washes with ethanol solution over three weeks until the solvent above the settled nanoparticles became clear. All D5 molecules are bound to TiO₂ NPs, with no extra D5 dye molecules present. Also, all samples were deposited by the drop casting method as stated in Chapter 2. As described in Chapter 3, section 3.2.5, measurements were conducted at the Surface and Material Science end station on the FlexPES beamline at the MAX IV synchrotron radiation facility in Sweden. The station uses a Scienta SES-2002 hemispherical analyser for photoelectron spectroscopy and a custom-built partial electron yield (PEY) microchannel plate detector for x-ray absorption measurements. Peak fitting was performed using the procedure described in Section 2. A linear or Shirley background

was removed before curve fitting. X-ray photoelectron spectroscopy (XPS) measurements at $h\nu = 600$ eV calibrated BE scales by matching the Ti $2p_{3/2}$ peak to 458.80 eV. The electronic properties of the D5 dye and its modified forms were analysed in this work using density functional theory (DFT) and time-dependent DFT (TD-DFT), respectively. During the procedure, computations of the electrical structure and geometry optimisation were performed. The ground-state geometries of isolated dyes and dye complexes were improved by using the B3LYP hybrid functional, which offers a balance between precision and computational efficiency for organic systems. This function was used to meet the requirements of the optimisation process.

Electronic structure analysis was carried out to determine the frontier molecular orbitals (HOMO and LUMO). The natural bond orbital (NBO) method was used to analyse the electron density distribution and assess the effects of electron-donating and electron-withdrawing substituents [58].

4.4.2 Results and Discussion

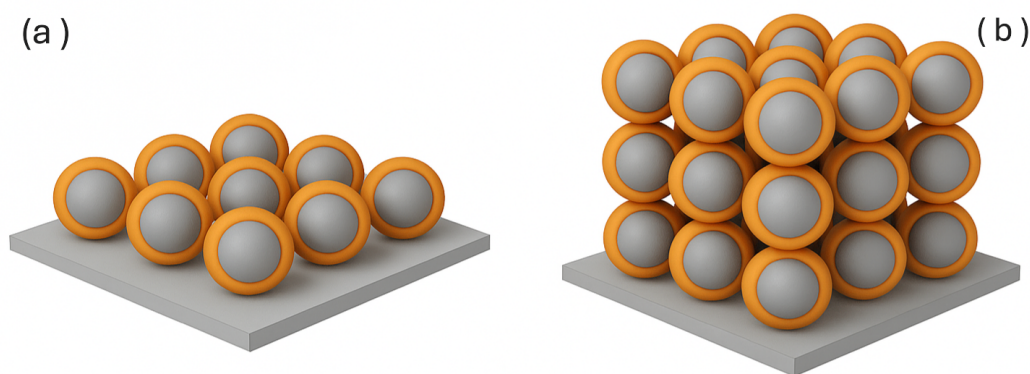


Figure 4.9: Schematic of TiO₂ NPs thickness where (a) is a thin film of TiO₂ NPs coated with a monolayer of D5 molecule, (b) a multilayer of TiO₂ NPs, each NP coated with a layer of D5 molecule. This represents this study.

The O $1s$ XPS spectra of D5 coated on TiO₂ NPs in Figure 4.10 demonstrate distinct characteristics that vary with coverage. four peaks are identi-

fied at binding energies of thin coverage and thick coverage TiO₂ nanoparticles, and bulk D5 on Au(111), as summarized in Table 4.5: Ti–O at 530.05 eV, Ti–OH at 531.3 eV, COO[−] at 531.8 eV, and C–OH at 533.06 eV, which includes a wide component associated with surface contamination in the range of 532 – 534 eV. The Δ BE between COO[−] and C–OH is 1.3 eV, with an area ratio of COO[−]:C–OH around 2:1, signifying partial deprotonation and a combination of chemisorbed and physisorbed states. The existence of Ti–OH indicates surface hydroxylation, potentially arising from the adsorption-induced dissociation of carboxylic acid protons which consist with [70]. The study of L0 molecules on a mesoporous titanium dioxide indicates that Ti–OH constituents are included in the O 1s envelope, attributed to either dissociated protons or surface hydroxyls [30]. With thick coverage, the C–OH peak disappears; however, Ti–OH, COO[−], and Ti–O continue, and the contamination signal is removed. This condition signifies total deprotonation and robust bidentate coordination of D5 to the TiO₂ NPs surface.

This interpretation is consistent with earlier results. On rutile TiO₂(110) at D5, a COO[−] peak at 531.8 eV is observed at a low deposition time of 5 minutes, indicating complete deprotonation. At thick coverages (20 – 40 min), supplementary peaks at C=O (532.6 eV) and C–OH (533.9 eV) appear with a 1:1 ratio and a 1.3 eV separation, signifying multilayer development [22]. The L0 measurements indicate C=O at 531.9 eV and C–OH at 533.3 eV, with a Δ BE of around 1.4 eV, suggesting partial deprotonation or mixed bonding geometries [30]. Together, these studies confirm that D5 on TiO₂ NPs loses some protons when there are few nanoparticles, but as more particles are added, it fully loses protons and forms a strong two-point attachment.

XPS

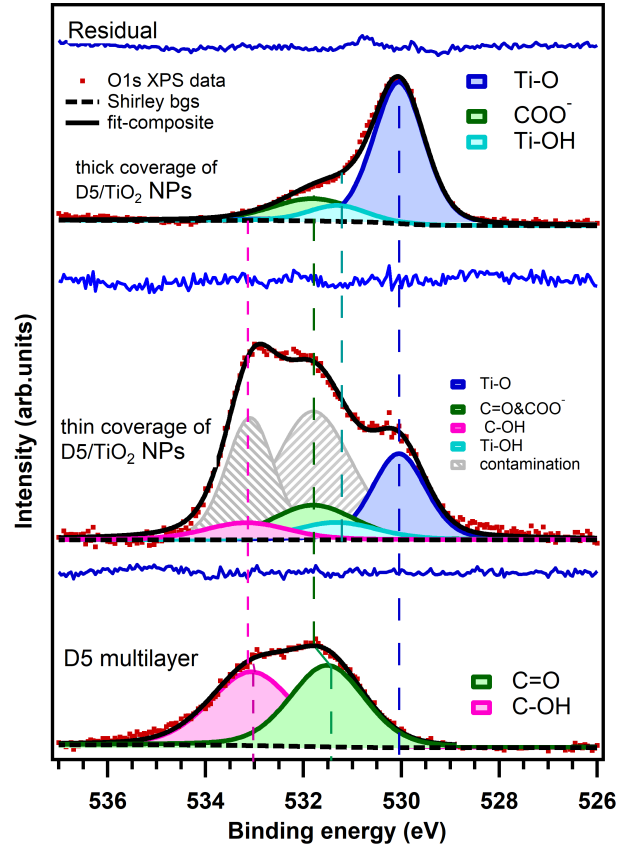


Figure 4.10: O 1s XPS spectra for thin and thick TiO_2 nanoparticles after coating with a D5 molecular monolayer, compared with bulk D5 on Au(111).

Table 4.5: A summary of the XPS component binding energies for O 1s of D5 on TiO_2 NPs surface.

peak	thin/thick	Δ (eV)	area ratio	Bulk D5 on Au(111)	Δ (eV)
TiO_2	530		2		
Ti-OH	531.3	1.3	1		
C=O & COO^-	531.8	1.3	2		
C-OH	533.06	3.1	1	533.06	
C=O				531.5	1.5

The C 1s spectra of the D5 dye on TiO_2 nanoparticles, shown in Figure 4.11, consist of four components, consistent with earlier studies on D5 and similar dyes such as L0[22, 30]. The main peak at 284.9 eV indicates carbon atoms in aromatic C-C structures, while there are other peaks at 285.6 eV for C-N

in the triphenylamine group, 286.6 eV for thiophene, and 288.6 eV for COO[−]. The peak positions and associated areas determined by the curve fitting are given in Table 4.6. In D5 multilayer and thick coverage of D5/TiO₂ NPs, a higher binding energy peak appears at 289.1 eV and is attributed to the carboxylic acid (COOH) functionality.

In the isolated D5 multilayer spectrum, a clear peak, shaded in grey in Fig. 4.11, appears at a higher binding energy (290 eV), beyond the COOH signal. This peak does not match any expected part of the D5 molecule, so it is likely due to contamination from carbon materials that were deposited on the surface during sample preparation or that were exposed to the air. The thin coverage, the C 1s spectrum is dominated by the aromatic C–C component, while the COO[−] contribution appears only as a very weak but discernible feature. Its low intensity is consistent with partial deprotonation of the carboxylic groups at the TiO₂ surface. No additional contaminant component was included in the fit. In the thick film, the C–C peak intensity is much higher at 27.8% than the expected molecular ratio of about 22%, indicating that there may be more layers covering the surface or some extra contamination.

This finding matches earlier reports that show dye molecules that are loosely attached can significantly increase the C–C signal [102]. Interestingly, this study found no shake-up features in either the thin or thick D5 films, which is different from earlier findings for L0 dye that showed shake-up structure between 290 – 292 eV [30]. No shake-up features were observed in either the thin or thick D5 coverage. The C 1s spectra were acquired with an overall energy resolution of ~ 1.3 eV (FWHM), which is sufficient to resolve shake-up satellites typically reported around 290–292 eV; their absence therefore suggests that significant π – π^* excitations are not present under the present conditions. Previous studies have reported very similar differences in binding energy between the prominent peaks (C–C, C–N, thiophene, and COOH) [22]. For instance, the energy gap between the C–C and COOH peaks is around 4.2

eV, which matches the results from studies on benzoic acid and other molecules with carboxylic groups on TiO_2 surfaces [28].

Overall, the data indicate that surface coverage, contamination, and fitting limits all influence the spectral profile, and that it is important to carefully separate chemisorbed and physisorbed species, especially for complex dye molecules.

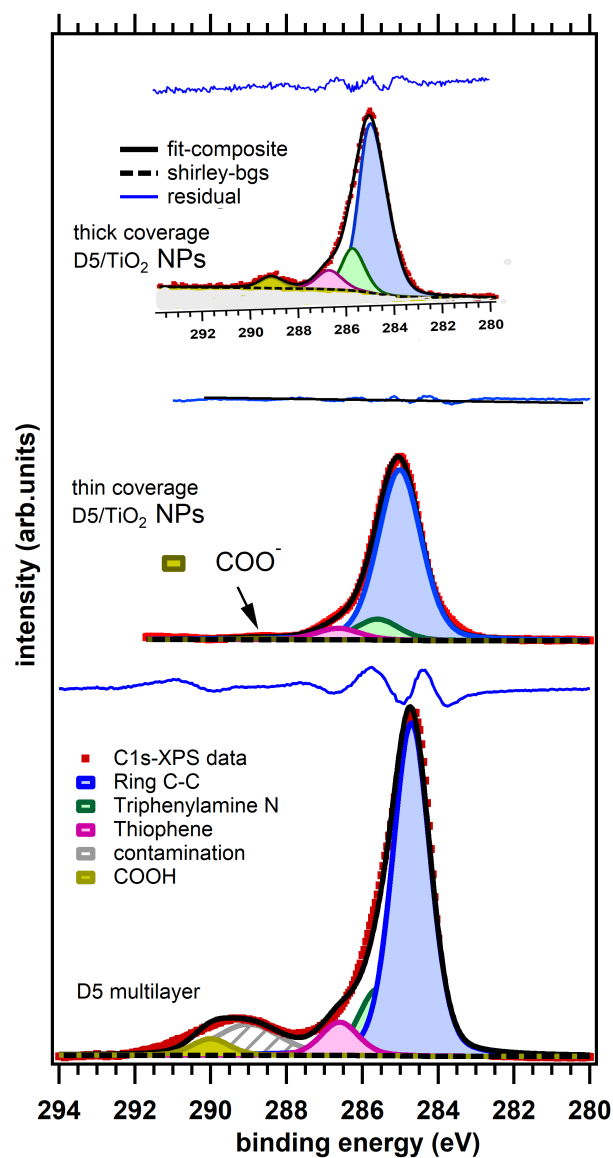


Figure 4.11: C 1s XPS spectra of D5 isolated and thin & thick coated on TiO_2 NPs.

Table 4.6: Summary of binding energy (BE) positions, energy shifts Δ relative to the lowest BE peak, and relative peak intensities (normalised to the main C–C component) for the C 1s components.

peak	BE	Δ (eV)	Peak area		
			D5 multilayer	thin	thick
Ring C–C	284.9		19.2	20.1	27.8
Triphenylamine N	285.6	0.7	3.5	4	5.6
Thiophene	286.6	1.7	1.9	2	1.8
COO [−]	288.6	3.7	1		
COOH	289.1	4.2	1		1

The N 1s XPS spectra of thin and thick D5 layers on TiO₂ nanoparticles, together with the D5 multilayer, are presented in Figure 4.12. In all cases, the N 1s region is resolved into two contributions associated with the nitrile (C≡N) group and the triphenylamine (TPA) moiety. In the present D5/TiO₂ NP system, the binding energies listed in Table 4.7 place the nitrile nitrogen at 399.04 eV for thin and thick coverages and at 398.5 eV for the D5 multilayer, whereas for the TPA nitrogen, the BEs are 400.0 eV thin/thick and 399.45 eV multilayer. The peak separations are approximately 1.0 eV, aligning with previously reported values for D5 [22, 103] and L0 [30] on TiO₂(110). The measured area ratios of nitrile to TPA differ from the expected 1:1. The ratios are 1:2.9 for thin coverage, 1:3.6 for thick coverage, and 1:3.7 for multilayer D5. The measured values correspond to those noted for L0, where a typical TPA: nitrile ratio of 3:1 or higher is associated with partial attenuation of the nitrile group, due to molecular configuration anchoring through the carboxylic acid end, resulting in a portion of the nitrile being hidden. The L0 analysis confirms the BE positions and changes in the N 1s signals for D5, explaining the molecular configuration and interactions with the surface in the D5/TiO₂ NPs system at different coverage levels.

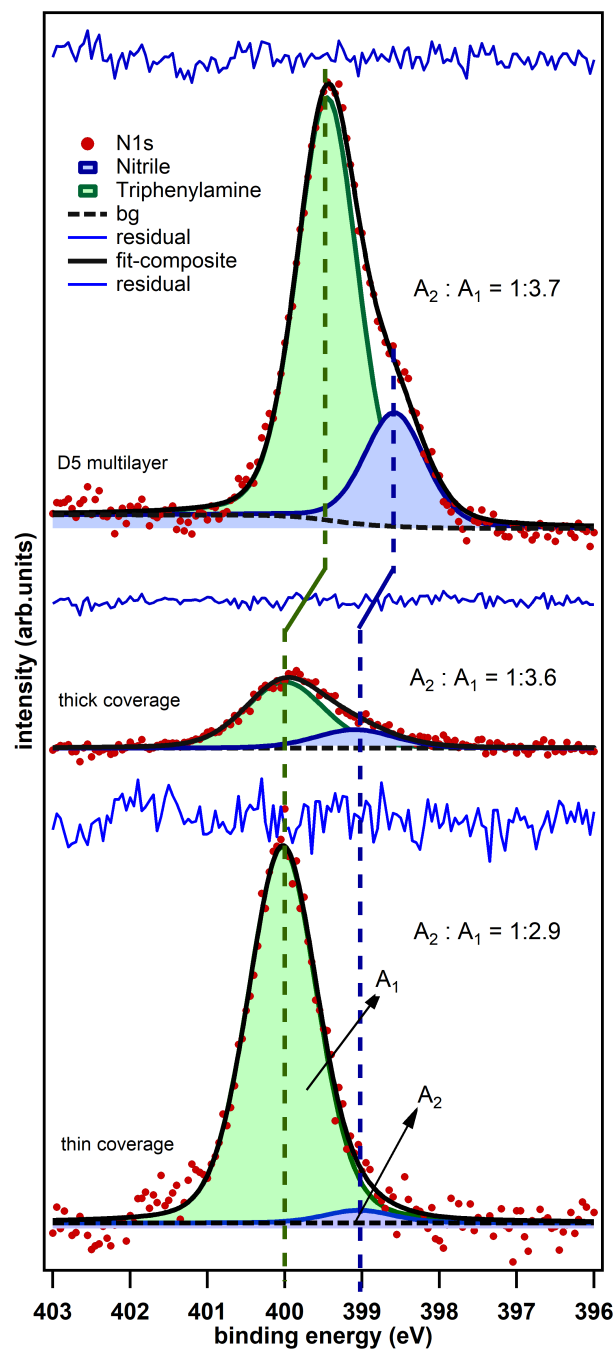


Figure 4.12: N 1s XPS spectra of isolated D5, and of thin and thick TiO₂ nanoparticles coated with a D5 molecular monolayer.

Table 4.7: A summary of the BE position to each peak for N 1s components.

peak	thin/thick	D5 multilayer
Nitrile N	399.04	398.5
Triphenylamine N	400	399.45

Figure 4.13 shows the S 2*p* XPS spectra for thin and thick TiO₂ nanoparticles coated with a D5 monolayer, together with the D5 multilayer. The spectra display two narrowly separated peaks approximately 1.2 eV with an intensity ratio of 2:1. The S 2*p*_{3/2} binding energies were measured at 164.3 eV and 164.19 eV, respectively. This configuration indicates that the thiophene sulphur atoms have a similar chemical environment, suggesting that the sulphur does not exhibit strong interactions with the TiO₂ NPs surface. The absence of significant broadening or energy shifts suggests that the interaction remains weak or stable, regardless of film thickness or layer count. This finding matches the literature review [22, 100, 103].

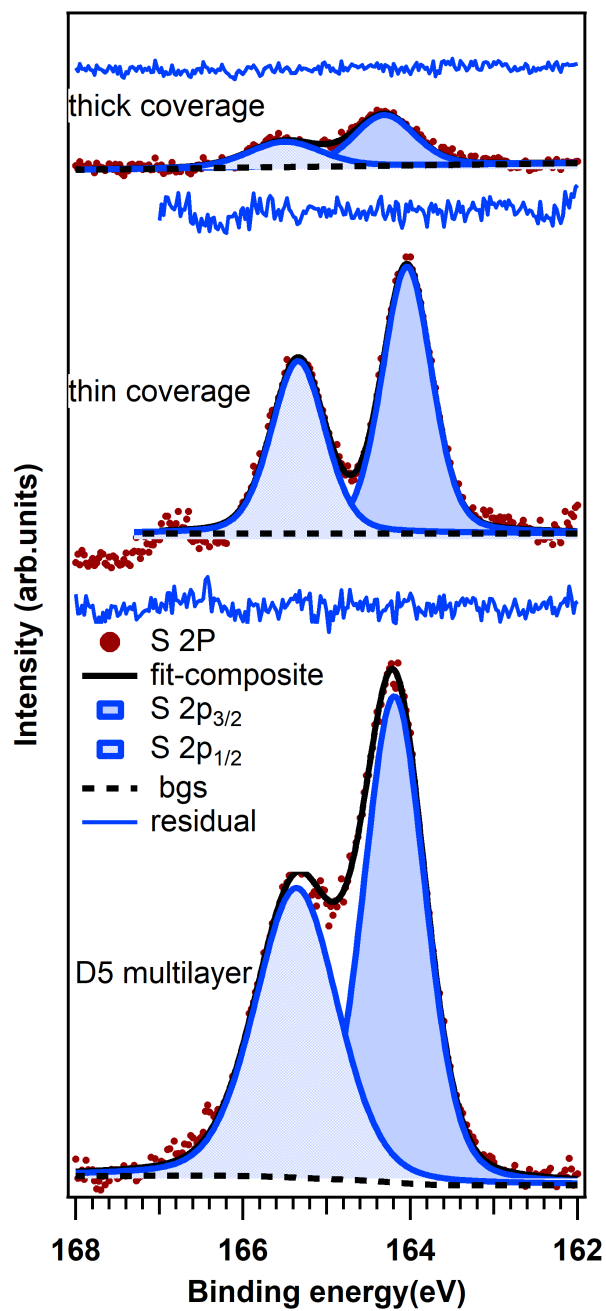


Figure 4.13: S 2*p* XPS spectra of isolated D5, and of thin and thick TiO₂ nanoparticles coated with a D5 molecular monolayer.

Table 4.8: A summary of the BE position to the thiophene peak for each coverage.

Peak	thin/thick	D5 multilayer
thiophene S 2 <i>p</i> _{3/2}	164.3	164.2
thiophene S 2 <i>p</i> _{1/2}	165.5	165.4

4.4.3 Electronic structure

Ground state molecular orbitals relevant to the spectroscopy discussed below are illustrated in Figure 4.14. The Kohn-Sham orbitals of an isolated D5 molecule show mainly delocalised frontier orbitals, with the HOMO and LUMO linking the acceptor and donor molecular components. The HOMO (orbital 117) exhibits increased density on the donating triphenylamine. In contrast, the LUMO (orbital 118) displays density biased towards the cyanoacrylic acid, with both possessing π/π^* lobes orientated out of the plane. The LUMO+1 to LUMO+7 (not shown) all contribute to the delocalised out-of-plane π system distributed throughout the molecule. The LUMO+8 (orbital 126) is the first electronic orbital exhibiting significantly distinct characteristics, featuring extensive in-plane lobes that are predominantly localised on the cyanoacrylate acid. This corresponds with the descriptions given elsewhere [43].

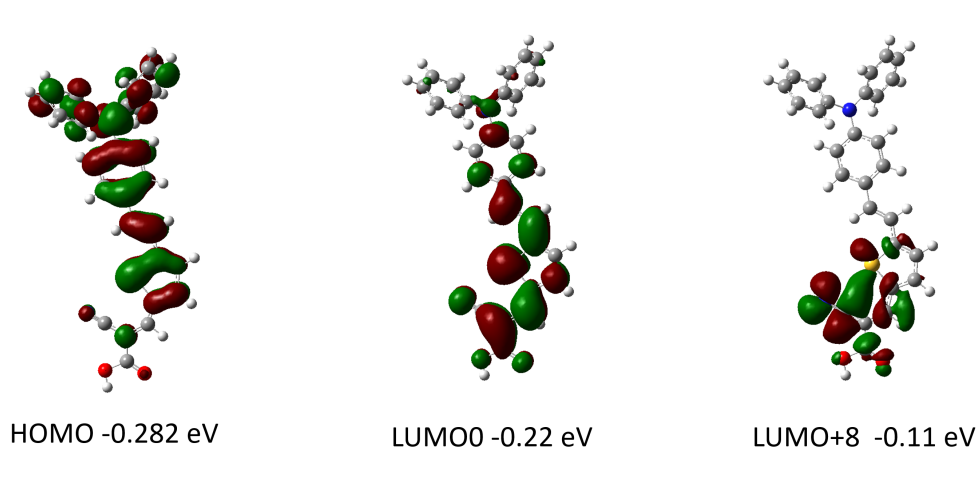


Figure 4.14: Specified ground state molecular orbitals generated by DFT. The LUMO and LUMO+8 primarily determine the most intense $N\ 1s \rightarrow \pi^*$ transitions.

Figure 4.15(a) displays a “density of states” diagram for thin coverage of thin D5 on TiO₂ NPs and D5 multilayer. The NEXAFS spectrum was aligned to the valence-band XPS energy scale using the procedure described in Section 3.3.1. Where the energy parameters are illustrated in Figure 4.15(b). The $N\ 1s$ XPS spectrum of this molecule (Table 4.7) shows two distinct peaks. The

N 1s orbitals associated with atoms in the nitrile and triphenylamine moieties exhibit binding energies as stated in Table 4.9.

Both N 1s peaks (nitrile and triphenylamine) must be considered. Figure 4.15 presents two NEXAFS spectra, where the solid line corresponds to unoccupied states and the other NEXAFS spectrum is shifted to align with the relevant optical HOMO-LUMO gap. The required shift was determined from the energy difference between the N 1s onset in NEXAFS and the reference binding energy obtained from XPS, and the spectrum was rigidly shifted by this value. The binding energy values have been obtained from Figure 4.15(a) 4.16 and listed in Table 4.9.

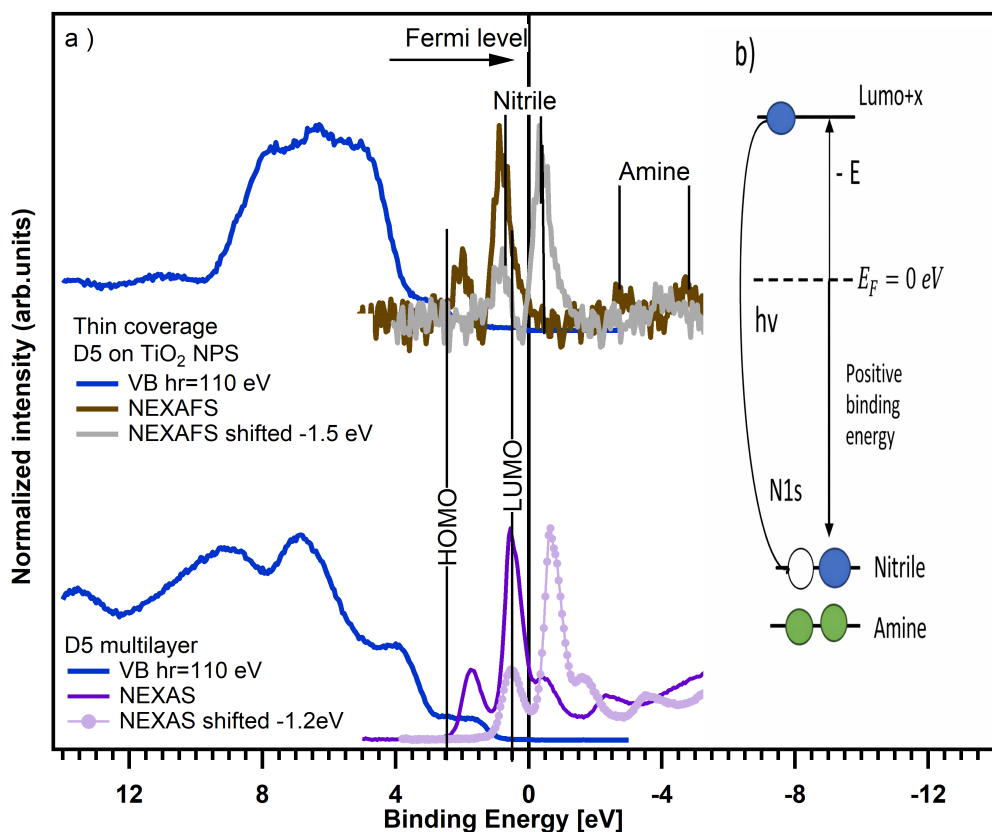


Figure 4.15: (a) A “density of states” graph illustrating the valence band (XPS) and unoccupied states (N 1s NEXAFS) along the same binding energy axis. (b) A diagram clarifying the meaning of the binding energy scale.

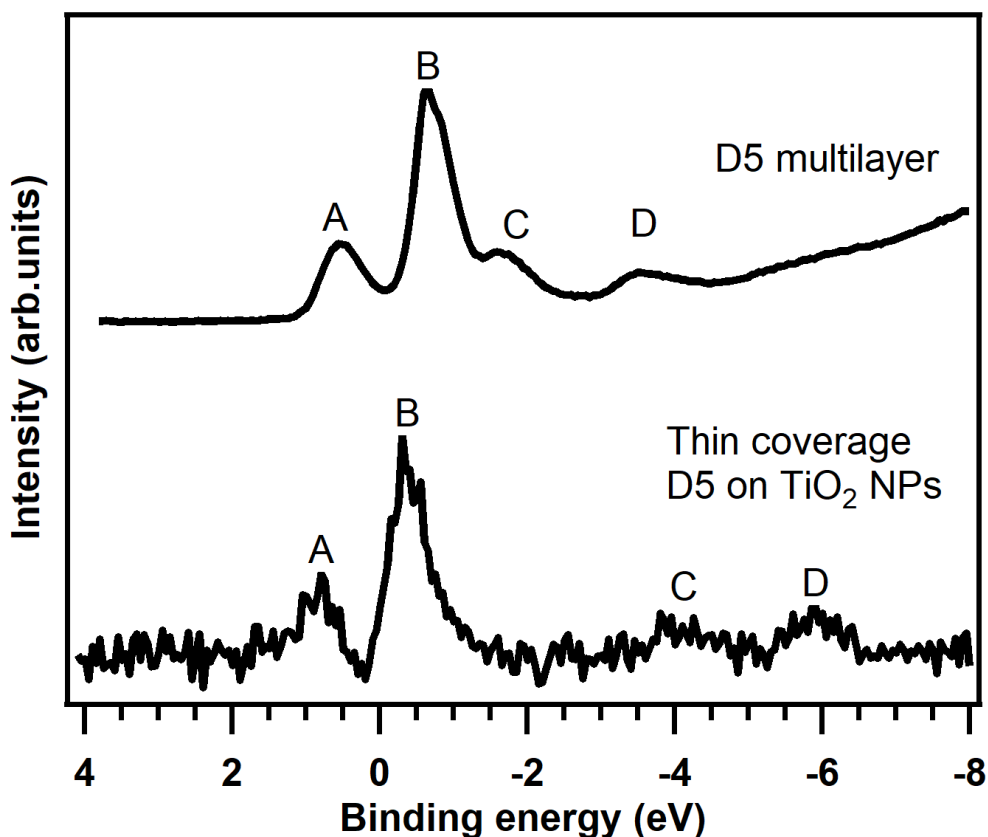


Figure 4.16: NEXAFS spectra in the fourth binding-energy region for thin D5 coverage on TiO₂ nanoparticles compared with the D5 multilayer. The spectra are aligned using the DoS plot, showing the energy shift of the LUMO+3 and LUMO+4 states.

The HOMO level is located at 2.5 eV for both coverages. The LUMO orbitals are labelled as A–D, where orbital A corresponds to the main LUMO and is used to define the HOMO–LUMO energy alignment. The energy gap in the core–excited state is approximately 2 eV for the D5 multilayer and 2.2 eV for thin D5 on TiO₂ nanoparticles, consistent with previous reports [104]. For thin coverage, the LUMO features (A–B) are attributed to the nitrile (N≡C) group, appearing at 0.7 eV and –0.3 eV, while the weaker peaks (C–D) at –4.1 eV and –5.8 eV originate from the amine TPA moiety of the D5 molecule, in agreement with earlier studies [30, 43, 99]. In the D5 multilayer, peaks A–B shift to 0.5 eV and –0.6 eV, whereas C–D are observed at –1.5 eV and –3.5 eV. The difference in the LUMO location between the D5 coverage on TiO₂ NPs and the D5 multilayer is due to the strong interaction between D5 and the

TiO₂ substrate, which shifts the energy levels. Both samples of D5 have the HOMO at 2.5 eV, and we label the LUMO orbitals (A–D), with A representing the LUMO. This LUMO helps set the energy difference between the HOMO and LUMO in the core–excited state, which is 2 eV for the D5 multilayer and 2.2 eV for thin D5 on TiO₂ NPs, matching what other studies have found [104]. In the thin layer, the LUMO (A–B) represents the nitrile $\text{N}\equiv\text{C}$ and is located at 0.7 and -0.3 eV, while the LUMO (C–D) has smaller peaks at -4.1 eV and -5.8 eV, which are caused by amine TPA in D5 molecules, as shown in other studies [30, 43, 99]. In D5 multilayer, the (A–B) are located at 0.5 eV and -0.6 eV, and C–D are located at -1.5 eV and -3.5 eV. The difference in where the LUMO is located between a thin coverage of D5 on TiO₂ NPs and in a D5 multilayer happens because D5 on TiO₂ NPs interacts strongly with the TiO₂ surface, which shifts the energy level [18]. The NEXAFS spectra shown in Figure ?? correspond to the fourth binding-energy region for both thin D5 coverage on TiO₂ nanoparticles and the D5 multilayer. The energy positions of the features (A–D) were determined from the density-of-states (DoS) analysis.

Table 4.9: The energies of the fourth XAS features (A–D), as indicated in Figure 4.16, are derived from the DoS plot in Figure 4.15, presented on the binding energy (BE) scale. The Δ (eV) values indicate the energy separation between the HOMO level and each corresponding LUMO state after energy alignment.

Feature	D5 multilayer(eV)	Δ (eV)	thin coverage(eV)	Δ (eV)
HOMO	2.5		2.5	
(A) LUMO	0.5	2	0.7	2.2
B	-0.6	3.1	-0.3	2.8
C	-1.5	4	-4.1	6.6
D	-3.5	6	-5.8	7.3

4.4.4 Resonant photoemission (RPES)

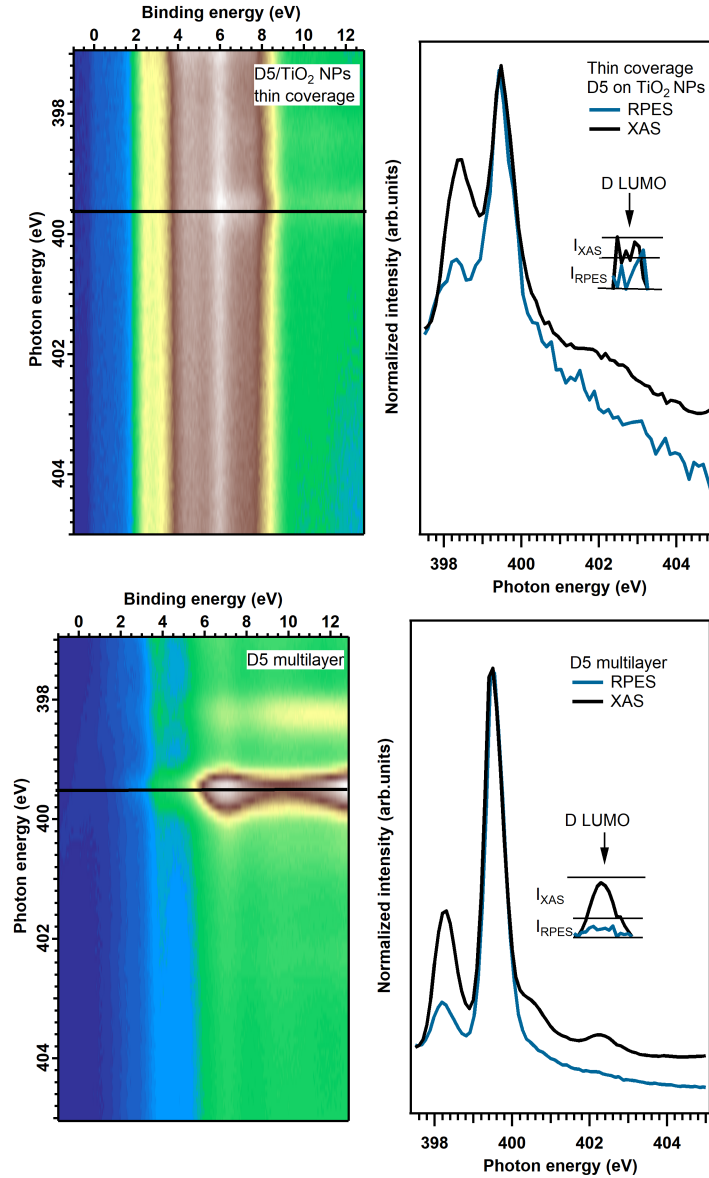


Figure 4.17: Resonant photoemission spectroscopy (RPES) maps recorded across the N 1s XAS resonance for D5 thin coverage on TiO_2 nanoparticles (top) and the D5 multilayer (bottom). The RPES intensity profiles were obtained by integrating the photoemission signal within the 5.5–6.5 eV binding-energy window to highlight the resonant contribution of the LUMO-related states.

The upper panel of Figure 4.15 shows the RPES resonance map of thin D5 coverage on TiO_2 nanoparticles, while the lower panel presents the corresponding RPES map of the D5 multilayer. The charge-transfer time from the D–LUMO

to the substrate conduction band is evaluated using the core-hole clock approach. The LUMO (A-D) of each D5 dye coverage facilitates charge transfer upon excitation. A result of a core-hole in RPES prevents the direct examination of the A LUMO, because it lies within the TiO₂ band gap of the core-excited system. However, the LUMO (B, C, and D) of each coverage seems to exist on the nitrile ligands. Therefore, the interaction of these orbitals with the substrate, and thus the associated charge-transfer dynamics, will be similar. The core-hole clock implementation of RPES utilises the principle that charge transfer must compete with the de-excitation of the excited state via resonant photoemission or resonant Auger processes.

The electron injection time is evaluated using the RPES core-hole clock methodology described in detail in Section 2.4. Only a summary is provided here: the analysis relies on the intensity ratios between the monolayer and multilayer RPES signals, normalised to the corresponding NEXAFS cross sections, together with the N 1s core-hole lifetime (6 fs for N₂) to quantify the charge-transfer dynamics.

The upper panel of Figure 4.17 shows the resonance map of a thin D5 coverage on TiO₂ NPs computed with the D5 multilayer; the bottom figure shows the resonance map of a thin D5 coverage on TiO₂ NPs computed with the D5 multilayer. The charge-transfer duration from D LUMO to the substrate's conduction band is computed using the core-hole clock implementation. The computed relative intensities of the participatory channel in the RPES, expressed as a proportion of the total X-ray absorption for D LUMO, is $I(\text{mono}_{\text{RPES}})/I(\text{mono}_{\text{NEXAFS}}) = 0.01 \pm 0.2$. The intensity ratios are extracted from the integrated, normalised peak areas of the RPES and XAS signals within the D-LUMO region, rather than from the peak heights shown in the zoomed inset. At the same time, the equivalent value for D5 multilayer is $I(\text{multi}_{\text{RPES}})/I(\text{multi}_{\text{NEXAFS}}) = 0.13 \pm 0.2$. The charge transfer duration from D LUMO

to the conduction band of TiO₂ NPs is found to be 0.5 ± 0.2 fs. It is expected because the previous study of D5 on TiO₂ found that the core-hole lifetime is in the femtosecond range [43].

4.5 Summary and Conclusions

In this chapter, we provide a detailed description of the D5 dye on three different types of TiO₂: crystal surfaces (110), mesoporous TiO₂, and nanoparticles (NPs). XPS, NEXAFS, and RPES were used to investigate them; the last two techniques were applied only to D5 on TiO₂ NPs. The key observation of D5 on (110) in this study was that ESD deposition over time (20, 40, 60 minutes) was observed when the ion gate was on at 20 and 40 minutes. The D5 molecule is bonded to TiO₂(110) through the COOH group after deprotonation, together with a C–OH hydrogen bond. There is no difference between ESD deposition and the situation when the ion gate is on; however, this type of deposition allows ions to pass through the surface more effectively. In the second study, HAXPES was used, resulting in similar probing depths for both monolayer and multilayer coverages. Consequently, no significant intensity difference was observed, and the spectral features appeared characteristic of a monolayer.

XPS measurement indicates that D5 binds to mesoporous TiO₂ via deprotonation of the COOH group together with a C–OH hydrogen bond. Additionally, the nitrile N≡C in a multilayer is shifted to lower energy; this shift may occur because molecules in a multilayer can interact differently with the surface or with each other than those in a monolayer. The third study involved D5 on TiO₂ nanoparticles and exhibited the same bonding behaviour as observed in the previous two studies, except that C–OH undergoes complete deprotonation at high coverage. The DFT study helps us visualise the electronic structure of D5, where the HOMO is located on the triphenylamine and the LUMO on the thiophene group. Based on the calculated energy-level alignment, where the NEXAFS spectrum is plotted on the same binding-energy

scale, show that the nitrile LUMO is located under the Fermi level, which is consistent with the DSSC charge-injection mechanism, where the LUMO orbital overlaps with the conduction band of TiO_2 , enabling fast charge transfer. From RPES data, we calculate the core-hole lifetime for D LUMO to be 0.5 ± 0.2 fs.

Chapter 5

Adsorption Geometry of N3

Dye on TiO₂(110) Surface

Investigated by XSW Technique and DFT calculations

5.1 Introduction

Understanding how the N3 dye binds to TiO_2 surfaces is essential to improving the efficiency of solar cell devices. In Chapter 3, we discuss the N3 dye on three types of TiO_2 surfaces: rutile single-crystal (110), mesoporous, and nanoparticles. We employed various techniques, including XPS, NEXAFS, and RPES. Those techniques help us understand electronic properties and chemical bonding at the interface. However, the NIXSW technique is a powerful method for calculating the positions of the atoms in the N3 molecule using coherent position, which tells us where the atom is and how it is ordered on the surface through the coherent fraction. In our case, the centre of the molecule is the Ru atom, which can be determined accurately once the exact atomic position is identified. In this chapter, the results of a series of NIXSW measurements of the N3 dye on rutile $\text{TiO}_2(110)$ are presented, focusing on the adsorption heights of the Ru atom and the carbon atoms in the carboxylic and thiocyanate groups, with comparison to DFT calculations. Figure 5.1 illustrates the N3 molecule and its ligands on rutile single-crystal $\text{TiO}_2(110)$.

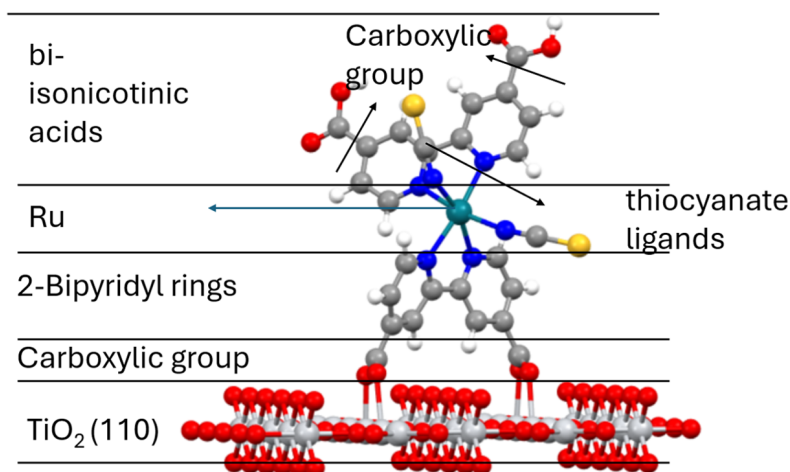


Figure 5.1: N3 molecule structure showing the labelled structural components, which are Ru centre, bi-isonicotinic acid, bi-pyridine ring, thiocyanate group, and carboxylic group. The substrate is rutile single $\text{TiO}_2(110)$.

5.2 Methodology

5.2.1 Sample preparation

The preparation and deposition were carried out in our laboratory at the University of Nottingham. The initial stage involved repeatedly cleaning the $\text{TiO}_2(110)$ substrate using sputtering with 2 kV Ar^+ ions for 20 minutes, followed by annealing at 600 °C, with repeated sputtering and annealing cycles until the C 1s XPS spectra indicated complete carbon removal. During each annealing stage, the Ti 2p core level was observed to confirm the restoration of surface defects and determine the presence of only Ti^{+4} oxidation states on the $\text{TiO}_2(110)$ surface. The rutile $\text{TiO}_2(110)$ substrate was prepared for the deposition of the N3 solution. The N3 solution was made by dissolving a small quantity of N3 dye in methanol.

In this experiment, we aimed to achieve a thin, homogeneous coverage, but uniform deposition was not achieved using electrospray alone. The sample was rastered within the electrospray beam to distribute deposition evenly across the 10×10 mm crystal surface. A C 1s XPS intensity map confirmed the uniformity, Figure 5.2. This chapter presents the XSW analysis, which determines the vertical positions of a chosen subset of atoms within the N3 dye. The locations of the central ruthenium atom and specific carbon atoms, such as those in carboxylate and thiocyanate groups, are identified in relation to the $\text{TiO}_2(110)$ surface. Other elements in the molecule, such as nitrogen or sulphur, were not identifiable within this dataset. The details of the XSW experiment setup can be found in Chapter 2.

5.2.2 NIXSW measurement

Normal-incidence X-ray standing wave (NIXSW) measurements were performed at the Diamond Light Source I09 beamline[105]. The rutile TiO_2 crystal was first aligned such that the incident X-ray beam satisfied the selected (hkl)

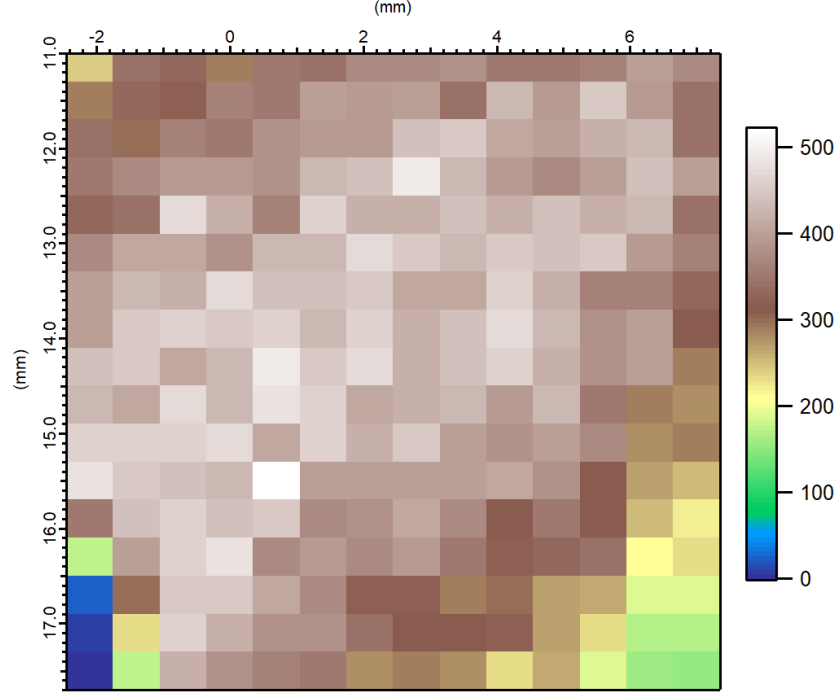


Figure 5.2: C 1s XPS intensity map of N3 dye deposited on $\text{TiO}_2(110)$ single crystal. The map demonstrates homogeneous coverage across the majority of the surface, with particularly uniform intensity at the centre. The horizontal axis corresponds to the x-position, and the vertical axis to the z-position. After XPS mapping, the sample was transferred to Diamond Light Source specifically for XSW measurements.

Bragg condition. Two specific rutile Bragg reflections, (hkl_1) , and (hkl_2) , were used to determine the positions of the adsorbate. Following alignment, the photon energy was scanned through the Bragg energy while the photoemission yield was recorded. As the Bragg condition was crossed, the phase of the standing-wave field shifted relative to the lattice planes, enabling determination of vertical adsorption heights from the coherent position and coherent fraction. The X-ray reflectivity and photoemission responses were fitted to extract both the coherent position, P_{hkl} , and the coherent fraction, F_{hkl} , for each scattering plane and element or species resolvable in the photoelectron spectra. NIXSW measurements were conducted at the (220) Bragg plane to determine the heights of the atomic positions across this plane.

5.3 Determination of Coherent Position and Coherent Fraction

The standing-wave XPS core-level spectra were imported into MATLAB for curve fitting. All of this was done to obtain an experimental value for the coherent position as well as coherent fractions. The core-level XPS spectra were fitted using a Voigt line shape, consisting of a convolution of Gaussian (instrumental resolution) and Lorentzian (lifetime) contributions. A Shirley background was applied to account for inelastic scattering. For each core level, chemically distinct components were included where necessary to reproduce the experimental line shape. The full-width at half maximum (FWHM) values were constrained consistently across equivalent components for the (220) lattice orientation.

5.3.1 XSW from the $\text{TiO}_2(220)$ reflection

Ru $3d_{5/2}$ core-level XSW from the $\text{TiO}_2(220)$ reflection

Figure 5.3 shows the $\text{TiO}_2(110)$ lattice geometry used in NIXSW measurements. Orange and violet mark the (220) and (110) Bragg planes. Inter-planar spacings are $D_{220} = 1.68 \text{ \AA}$ and $D_{110} = 3.2 \text{ \AA}$. The figure also shows the directions of incident and outgoing X-rays. They are parallel planes, so the angle between them is zero.

XPS was used to measure the core-level photoelectron spectra of the elements, while the XSW analysis was employed to determine their vertical positions relative to the crystal planes. Figure 5.4 shows the Ru $3d_{5/2}$ peak at a binding energy of approximately $\approx 271.5 \text{ eV}$, highlighted in yellow. The intensity variation of this peak across the Bragg scan Fig.5.4, (left) was fitted to determine the coherent position (P_c) and coherent fraction (F_c).

The left part of Figure 5.4 presents the XSW measurement of the TiO_2 at the (220) plane. The Table 5.1 provides all parameter values. We obtained the data at the (220) Bragg reflection at 3780 eV. The Gaussian broadening (SB) of

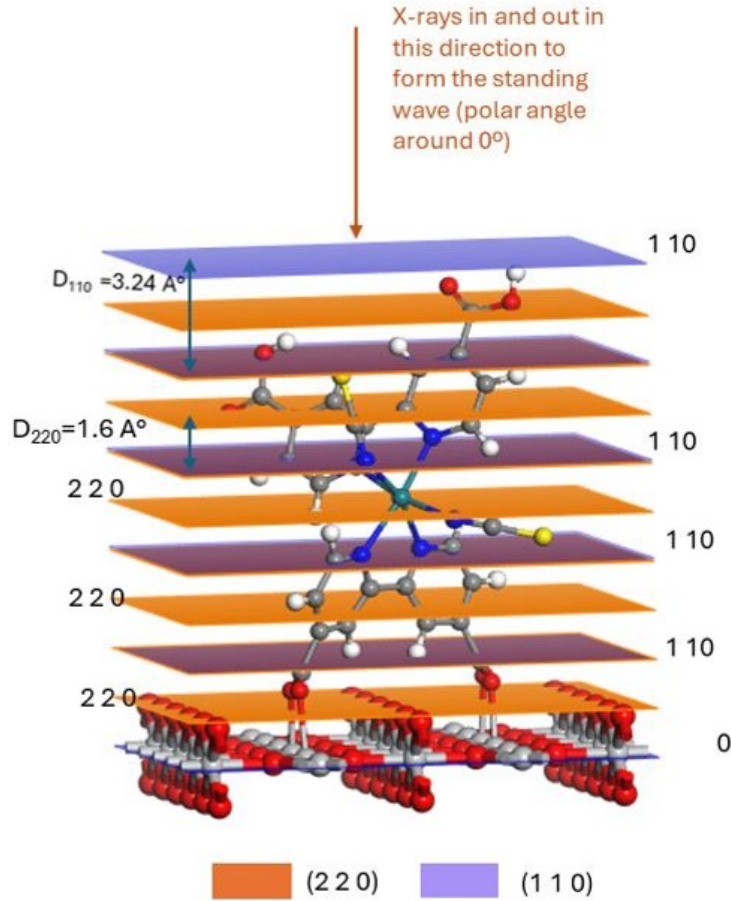


Figure 5.3: Schematic representation of the TiO₂(110) surface showing the (220) lattice planes in orange and the (110) planes in violet. The corresponding interplanar spacings are $d_{220} = 1.68 \text{ \AA}$ and $d_{110} = 3.2 \text{ \AA}$. X-ray standing wave (XSW) analysis of the Ru $3d_{5/2}$ core level yields a coherent position $P_c = 0.77$ and a coherent fraction $F_c = 0.22$ with respect to the TiO₂ (220) Bragg reflection. This corresponds to a fractional height of $z = 1.29 \text{ \AA}$ within one $d \cdot 220$ spacing. Using the relation $z = (P_c + n)d_{220}$, and considering $n = 4$ and $n = 5$, which are consistent with the expected adsorption height range, Ru adsorption heights of approximately $8.3 \text{ \AA}$ and $9.6 \text{ \AA}$ above the TiO₂(110) surface are obtained.

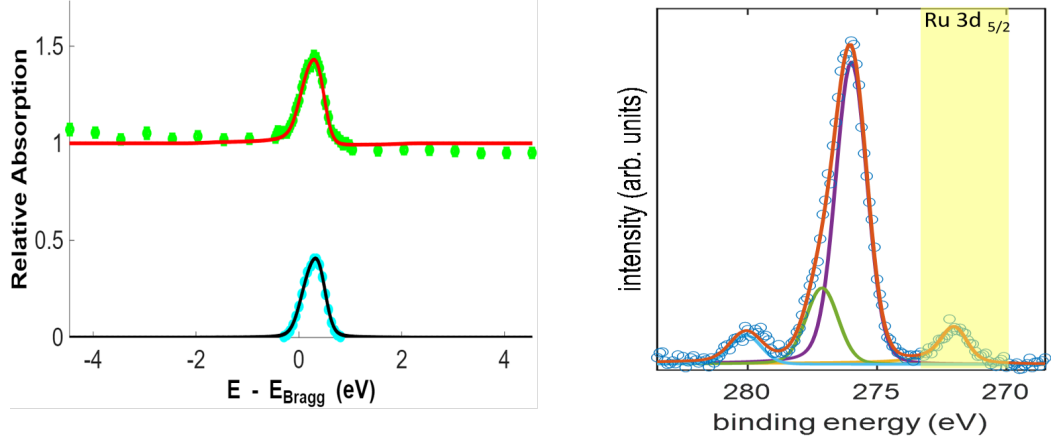


Figure 5.4: Right: XPS spectrum measured at the synchrotron beamline showing the Ru $3d_{5/2}$ peak at a binding energy of approximately 271.5 eV (highlighted in yellow). Left: NIXSW yield curve obtained from the photoelectron intensity of the Ru $3d_{5/2}$ core-level peak as a function of $E - E_{\text{Bragg}}$ for the $\text{TiO}_2(220)$ reflection (Bragg energy = 3780 eV). The solid red line represents the fit used to extract the coherent position (P_c) and coherent fraction (F_c).

the reflectivity peak is 0.19 eV, indicating a narrow peak width and suggesting good crystal quality and stable measurement conditions. From the fitting of XSW absorption, the P_c is 0.71, and a coherent fraction F_c is 0.22. The low F_c value suggests partial disordering and a possible distribution of molecular adsorption geometries or surface heterogeneity. The estimated height of this atom with respect to the (220) reflection is $= 1.29 \text{ \AA}$ above the TiO_2 surface. The z values from the coherent position represent only fractional positions within the (220) spacing. These will later be converted into realistic heights above the $\text{TiO}_2(110)$ surface by adding integer multiples of d_{220} 1.68 $\text{\AA}$.

It should be emphasised that the value of $Z = 1.29 \text{ \AA}$ corresponds only to the fractional position of Ru within the (220) interplanar spacing $P_c = 0.77$, $d_{220} = 1.68 \text{ \AA}$. To determine the realistic height above the surface, integer multiples of d_{220} must be considered. This yields possible Ru heights of 8.01 $\text{\AA}$ for $n = 4$ and 9.69 $\text{\AA}$ for $n = 5$. Therefore, the Ru atom is expected to lie within this range (8.01 $\text{\AA}$ –9.69 $\text{\AA}$), which is consistent with the adsorption geometry shown in Figure 5.3 and the DFT results.

C 1s atom at TiO₂(220) reflection

COOH group

The C 1s XPS spectrum exhibits a component at approximately 280 eV, which is assigned to the carbon atom of the COOH group. In the N3 molecule, four carboxylic acid groups are present; two are bonded to the TiO₂(110) surface, while the other two remain in the upper part of the molecule, as illustrated in Fig 5.1. To determine the vertical position of the carbon atoms associated with this spectral component, X-ray standing wave (XSW) measurements were performed using the TiO₂(220) Bragg reflection. Fitting the NIXSW profile of the C 1s component attributed to the COOH group yields a coherent position ($P_c = 0.69$) and a coherent fraction $F_c = 0.36$. The coherent position represents the average position of the emitting atoms relative to the (220) lattice planes, while the coherent fraction reflects the degree of vertical ordering.

The relatively low coherent fraction indicates partial ordering and suggests a distribution of adsorption geometries or molecular configurations on the surface. The coherent position corresponds to a fractional coordinate within the (220) plane spacing and can be converted to an absolute adsorption height by adding integer multiples of the interplanar spacing d_{220} .

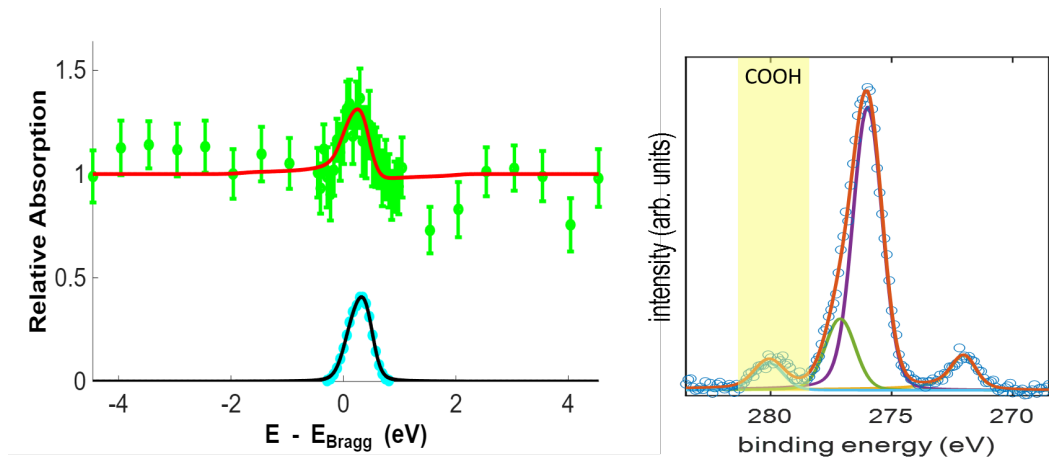


Figure 5.5: XPS and NIXSW analysis of the C 1s signal associated with the COOH group of the N3 molecule on $\text{TiO}_2(110)$. The right panel shows the C 1s XPS spectrum, where the highlighted component corresponds to the carboxylic acid carbon. The left panel shows the NIXSW yield measured across the $\text{TiO}_2(220)$ Bragg reflection (Bragg energy 3780 eV). Fitting the standing wave profile yields the coherent position and coherent fraction for this species.

NCS group

The right panel of Figure 5.6 shows the C 1s XPS spectrum, where a component appears at ≈ 277.5 eV and is assigned to the thiocyanate group (NCS). The thiocyanate ligand has the structure $\text{N}=\text{C}=\text{S}$, and in the N3 molecule, two NCS groups are present. One of these groups is expected to interact with the TiO_2 surface through the sulfur atom, placing it closer to the surface and therefore below the Ru centre, while the second group remains further from the surface.

The left panel of Figure 5.6 shows the NIXSW yield measured across the $\text{TiO}_2(220)$ Bragg reflection. From fitting the NIXSW profile, a coherent position $P_c = 0.62$ and $F_c = 0.27$ are obtained for the carbon atoms associated with the NCS component.

The relatively low coherent fraction indicates limited vertical ordering of the NCS groups with respect to the crystal lattice, suggesting a distribution of adsorption geometries or molecular orientations. The coherent position corresponds to a fractional coordinate within the (220) lattice plane spacing and can be converted into an absolute height by adding integer multiples of the

interplanar spacing (d_{220}). In the next section, we will compare these results with the DFT calculation at Z height.

NCS group

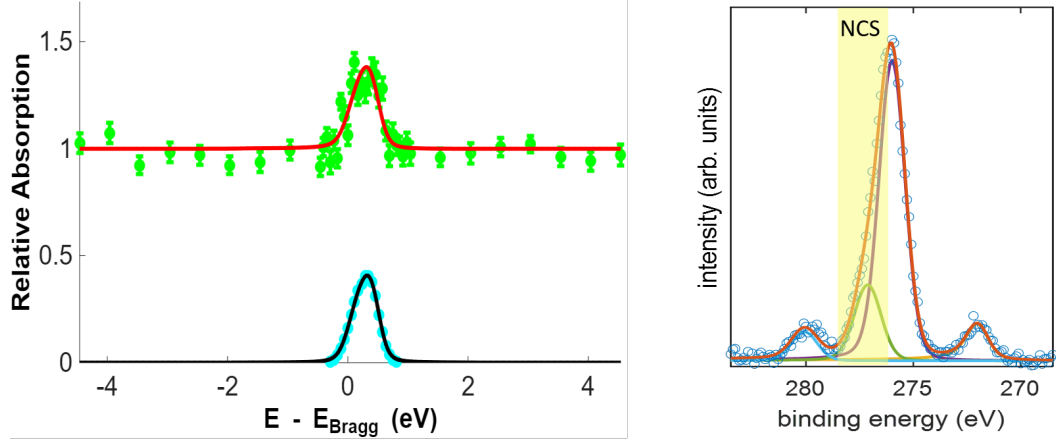


Figure 5.6: XPS and NIXSW analysis of the C 1s component associated with the NCS group of the N3 molecule adsorbed on $\text{TiO}_2(110)$. The right panel shows the C 1s XPS spectrum with the highlighted component corresponding to the NCS species. The left panel shows the NIXSW yield measured across the $\text{TiO}_2(220)$ Bragg reflection (Bragg energy 3780 eV). Fitting of the standing wave profile provides the coherent position and coherent fraction for this atomic species.

Table 5.1: The values in the table extracted from XSW figures confirmed the coherent position (P_c) and coherent fraction (F_c).

17.7					
Sp.	Refl. (hkl)	P_c	F_c	d (Å)	Z (Å)
Ru $3d_{5/2}$	(220)	0.77	0.22	1.68	1.29
COOH	(220)	0.69	0.36	1.68	1.15
CNS	(220)	0.62	0.27	1.68	1.04

The coherent fractions obtained for all species are relatively low ($F_c \leq 0.4$), indicating a significant distribution of adsorption heights or molecular orientations on the surface. In such cases, the coherent position should be interpreted as an

average position of the emitting atoms rather than a well-defined adsorption height.

5.4 XSW Measurements vs. DFT Predictions

The above section shows the three main parts of the N3 dye molecule using X-ray standing wave at the Ti(220) reflection. These parts were the ruthenium centre (Ru 3d), carboxyl groups (COOH), and thiocyanate ligands (NCS). By comparing the measured heights with DFT predictions, we confirmed the chemical structure and attachment mechanism, supporting our understanding of how the molecule binds to the rutile TiO₂(110) surface.

Figure 5.7 shows the N3 dye structure on rutile TiO₂(110), where the Ru is the centre of the molecule, for which the XSW exhibited its coherent position P_c of 0.77, corresponding to height Z_{220} of 1.29 Å relative to Ti(220) reflection. DFT calculations using geometry optimisation determined the three-dimensional atomic positions of all atoms in the N3 dye molecule adsorbed on the TiO₂(110) surface. From these calculations, the vertical heights (z-coordinates) of the ruthenium atoms in layers $n = 0$ to 6 were extracted. Comparison of the experimental XSW height with DFT-calculated values, as shown in Table 5.2, revealed the closest match between layers $n = 4$ (8.014 Å) and $n = 5$ (9.694 Å). The atomic-position analysis confirmed that the Ruthenium atom labelled Ru61 in the DFT model is located at 8.38 Å above the titanium surface, between the two layers. This agreement between theoretical predictions and experiments supports the computational model’s validity. The coherent fraction, $F_c = 0.22$, indicates a high degree of structural disorder in the ruthenium coordination environment.

Out of the four carboxyl groups (COOH), the two lower groups bound to the surface show a coherent position P_c of 0.69, corresponding to a height Z_{220} of 1.15 Å relative to the Ti(220) reflection. DFT geometry optimisation calculations revealed the three-dimensional positions of atoms in the N3 dye structure,

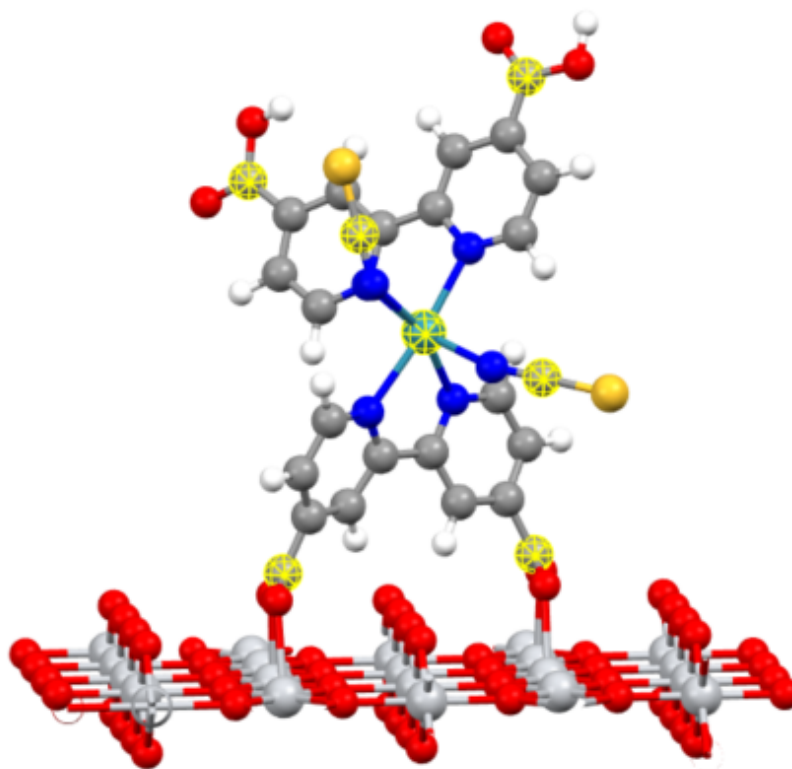


Figure 5.7: Optimized adsorption geometry of the N3 dye on the rutile $\text{TiO}_2(110)$ surface obtained from DFT calculations. The yellow circles highlight the atomic species analysed in the NIXSW measurements, namely the carbon atoms of the carboxyl (COOH) groups, the carbon atom of the thiocyanate (NCS) group, and the Ru centre. These atoms are used for comparison between the DFT-predicted positions and the experimental XSW results relative to the $\text{TiO}_2(220)$ lattice planes.

as shown in Table 5.2. The N3 molecule contains four carboxyl groups with clearly distinct heights: two act as surface anchors, while the other two extend over a bipyridine ligand. By comparing the experimental XSW data with DFT predictions at the $n = 1$ layer, the measured coherent position is consistent with the DFT-predicted height for the two surface-bound carboxyl groups within experimental uncertainty. The atomic positions of the carbon atoms (labelled C110 and C113 in the DFT model) at 2.8 Å are located very close to the TiO₂ surface to facilitate molecular bonding through bidentate coordination.

In the $n = 6$ and $n = 8$ layers, DFT calculations predict the positions of the upper carboxyl groups: the carbon atoms labelled C104 and C107 in the DFT model, located at 11.5 Å and 14.2 Å, respectively, located above the centre of the ruthenium. This vertical separation between the lower ($n = 1$) and upper ($n = 6$ and 8) carboxyl groups, with Ru at an average height (8.3 Å, between $n = 4$ and $n = 5$), strongly supports the conclusion that the Ru atom occupies the central region of the molecular structure.

The coherent fraction $F_c = 0.36$ is the highest among the three components, indicating partial disorder and/or the presence of multiple adsorption geometries for the carboxyl groups in line with their dual role in surface binding and structural extension. The thiocyanate (NCS) groups show a coherent position $P_c = 0.62$ and a coherent fraction $F_c = 0.27$, the lowest among the three measured components, indicating a higher degree of disorder, corresponding to a height Z_{220} of 1.0 Å for the Ti(220) reflection. The DFT geometry optimisation calculations revealed the three-dimensional positions of carbon atoms within the NCS groups, showing their asymmetric distribution relative to the TiO₂ surface, as illustrated in Table 5.2.

The N3 dye contains two thiocyanate ligands with significantly different orientations and surface interactions. By comparing the experimental XSW data with DFT predictions at the $n = 4$ layer, the carbon atom labelled C87 in the DFT model, belonging to one NCS group, is located $7.4 \text{ \AA}$ below the centre of the ruthenium atom at $8.3 \text{ \AA}$. This low position indicates that the sulphur atom in this NCS bond may have weak interactions with the titanium surface, bringing the entire bond closer to the substrate. In contrast, between $n = 5$ and 6 layers, the carbon atom C(90) from the second NCS group is located at $10.8 \text{ \AA}$, orientated above the centre of the ruthenium atom and away from the surface, without any binding interaction.

The asymmetric bonding, in which one thiocyanate molecule is anchored to the surface through sulphur interaction, explains the significant height difference observed between the two carbons in the NCS groups ($7.4 \text{ \AA}$ compared to $10.8 \text{ \AA}$). At the same time, the other remains freely extended in solution. The coherent fraction $F_c = 0.27$ indicates significant positional disorder, suggesting a broad distribution of adsorption geometries, which limits the interpretation of the coherent position as a well-defined height.

Table 5.2: N3 atomic heights relative to the $\text{TiO}_2(110)$ surface from DFT calculations. Atom labels (e.g., C87, Ru61) correspond to the atom indexing in the DFT model.

Group	Atom (DFT label)	Z ($\text{\AA}$)
Ru	Ru61	8.3 ± 0.07
NCS	C87	7.4 ± 0.11
NCS	C90	10.8 ± 0.11
COOH	C104	11.58 ± 0.11
COOH	C107	14.24 ± 0.12
COOH	C110	2.8 ± 0.12
COOH	C113	2.8 ± 0.12

Overall, the N3 molecular anchors on $\text{TiO}_2(110)$ by 2-M bidentate that shows through the two carboxyl groups near the $\text{TiO}_2(110)$ surface at the atomic layer $n = 1$, their height is $2.8 \text{ \AA}$ above $\text{TiO}_2(110)$ surface. The Ru atom is located in the centre of the molecule above the surface at $8.3 \text{ \AA}$ between the atomic layers $n = 4$ and 5 . The thiocyanate groups have a different environment, which is expected to have one bonded to the surface via the S atom and one nonbonded. The DFT results are consistent with the experimental data.

5.5 Summary and Conclusions

With continued study of N3, this chapter presents the result of N3 on rutile $\text{TiO}_2(110)$ as measured by the NIXSW technique. The chapter aims to determine the vertical positions of selected atoms within the N3 dye, including the central ruthenium atom and specific carbons in carboxylate and thiocyanate groups, relative to the $\text{TiO}_2(110)$ surface. XPS measurements identified three peaks in the C $1s$ spectrum: Ru $3d_{5/2}$, carbon in the COOH group, and carbon in the $\text{N}=\text{C}=\text{S}$ group of thiocyanate. The XSW technique calculated the coherent positions and fractions of these atoms relative to the $\text{TiO}_2(220)$ reflection. The main finding is that the Ru atom is located at the centre of the molecule, $8.38 \text{ \AA}$ above $\text{TiO}_2(110)$, corresponding to an atomic layer number between $n = 4$ and 5 .

The carboxylic groups may adopt multiple configurations: a lower height of $2.8 \text{ \AA}$, suggesting surface bonding via a bidentate mode, which is consistent with DFT predictions at atomic layer number $n = 1$, while DFT calculations suggest possible configurations at higher atomic layers $n = 6$ and $n = 8$. The thiocyanate groups yield a single coherent position in the XSW measurements, corresponding to an average height. The low coherent fraction indicates a distribution of adsorption geometries rather than distinct, well-resolved environments. These height measurements of both the COOH and thiocyanate groups are consistent with Ru being central in the N3 molecule and with N3

anchoring to $\text{TiO}_2(110)$ in a 2-M bidentate fashion, as discussed in Chapter 3. The DFT calculations support the interpretation of the experimental results, although the XSW measurements reflect averaged positions due to the low coherent fractions.

Chapter 6

Conclusion and future work

6.1 Conclusion

This thesis presents a detailed investigation of the bonding geometry, electronic structure, and charge-transfer dynamics of D5 and N3 dyes at TiO_2 interfaces using a combination of XPS, NEXAFS, RPES, and NIXSW techniques, supported by DFT calculations.

XPS measurements show that both N3 and D5 dyes bind to TiO_2 surfaces primarily through deprotonation of carboxylic acid groups, forming stable interfacial configurations across rutile $\text{TiO}_2(110)$, mesoporous TiO_2 , and nanoparticle systems. Additional interactions involving thiocyanate and nitrile groups suggest the presence of multiple possible adsorption configurations, depending on surface structure and molecular coverage.

NEXAFS and RPES measurements provide insight into the electronic structure and charge-transfer processes. For the N3 dye, the LUMO and partially the LUMO+1 states are located within the band gap of TiO_2 , limiting direct electron transfer, while higher unoccupied states (LUMO+2 and LUMO+3) overlap with the conduction band, enabling efficient charge transfer. RPES results indicate ultrafast charge transfer occurring within the core-hole lifetime. The charge-transfer time from the LUMO+3 orbital to the conduction band increases from 3 ± 0.02 fs for low coverage on TiO_2 nanoparticles to 18.7 ± 0.02 fs for thicker films on mesoporous TiO_2 , indicating reduced electronic coupling at higher molecular coverage.

For the D5 dye, similar adsorption behaviour is observed, with binding via deprotonated carboxylic groups. The electronic structure indicates favourable alignment of the LUMO with the TiO_2 conduction band, consistent with efficient charge injection. RPES measurements yield a core-hole lifetime of ap-

proximately 0.5 ± 0.2 fs, supporting rapid electron transfer at the interface.

NIXSW measurements provide structural information for the N3 dye on $\text{TiO}_2(110)$. The ruthenium atom is located at an average height of $8.38 \text{ \AA}$, consistent with its central position within the molecule. The carboxyl groups exhibit an average height of approximately $2.8 \text{ \AA}$, consistent with surface anchoring in a bidentate configuration. The thiocyanate groups yield a single coherent position corresponding to an average height. However, the relatively low coherent fractions indicate a distribution of adsorption geometries, and therefore the measured positions should be interpreted as average values rather than well-defined atomic positions.

Overall, the combined experimental and theoretical results provide a consistent description of dye adsorption and charge-transfer processes at TiO_2 interfaces. While DFT calculations suggest multiple possible adsorption configurations, the XSW measurements reflect averaged structural information due to the presence of disorder. These findings highlight the importance of molecular configuration, surface structure, and coverage in determining interfacial electronic behaviour in dye-sensitised systems.

6.2 Future work

6.2.1 Charge Transfer and Adsorption of N3 Dye on TiO_2 : Single Crystal, Mesoporous, and Nanoparticles

The N3 dye may be replaced with ruthenium-based dyes, such as N719 or Black Dye, in subsequent studies to improve these results. Using this method, researchers can directly evaluate the impact of specific carboxyl groups and ligands on charge-transfer rates, thereby identifying essential chemical char-

acteristics that directly influence efficiency. Researchers can also place these dyes on oxide surfaces, such as ZnO or SnO₂, to illustrate how the conduction band energy of each oxide affects electron injection.

The findings of these investigations will eventually contribute to the optimisation of dye-oxide pairings for improved device performance, highlighting the need to tailor materials to specific applications.

6.2.2 XPS, DoS and RPES Study of D5 Adsorbed on TiO₂ Surfaces

Since D5 demonstrated a rapid charge-transfer time of 0.5 fs, examining other triphenylamine-based dyes with alternative anchoring groups, such as phosphonic or hydroxamic instead of carboxylic, will help clarify how binding methods affect injection efficiency. Additionally, Scanning Tunnelling Microscopy will allow us to image individual molecules and assess their surface arrangement, providing insight into whether they aggregate or distribute evenly. This will help explain the observed changes in the nitrile spectrum at different coverages.

6.2.3 Adsorption Geometry of N3 Dye on TiO₂(110) Surface Investigated by XSW Technique and DFT calculations

To complete the three-dimensional structural analysis of the N3 molecule on the surface, additional Bragg reflections, such as (111) and (002), should be used alongside the current (220) measurement. This approach will more precisely determine atomic positions. Applying the same method to the D5 dye will enable a direct comparison of adsorption geometries between organic and metal-based dyes, clarifying the relationship between molecular structure and surface binding. Further studies on the geometries of dye adsorption could provide deeper insights. Future beamtime will allow us to compare two dyes similar to N3, one with carboxylate anchor ligands and one without. This will probe the role of the anchoring group in charge transfer. In addition, XSW

can be employed to determine the Ru height above the TiO_2 surface, which is expected to be closer to the surface when the dye lacks carboxylic groups.

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