Molecular Interaction of Thin Film Photosensitive Organic Dyes on TiO$_2$ Surfaces

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Doctoral Thesis
Stockholm, Sweden 2011
Akademisk avhandling som med tillstånd av Kungl Tekniska högskolan framlägges till offentlig granskning för avläggande av Teknologe Doktorsexamen i Mikroelektronik och tillämpad fysik fredagen den 02 december 2011, klockan 10.00 i Sal C2, KTH-Electrum, Isafjordsgatan 26, Kista, Stockholm.

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Tryck: Kista Snabbtryck AB
Abstract

The photosensitive molecule adsorption on titanium dioxide (TiO₂) forms the so-called “dye sensitized TiO₂” system, a typical organic/oxide heterojunction, which is of great interest in catalysis and energy applications, e.g. dye-sensitized solar cell (DSSC). Traditionally, the transition metal complex dyes are the focus of the study. However, as the fast development of the organic semiconductors and invention of new pure organic dyes, it is necessary to expand the research horizon to cover these molecules and concrete the fundamental understanding of their basic properties, especially during sensitization.

In this work, we focus on two different photosensitive molecules: phthalocyanines and triphenylamine-based dyes. Phthalocyanines are organic semiconductors with symmetric macroaromatic molecular structures. They possess good photoelectrical properties and good thermal and chemical stability, which make them widely used in the organic electronic industries. Triphenylamine-based dyes are new types of pure organic dyes which deliver high efficiency and reduce the cost of DSSC. They can be nominated as one of the strong candidates to substitute the ruthenium complex dyes in DSSC. The researches were carried out using classic surface science techniques on single crystal substrates and under ultrahigh vacuum condition. The photosensitive molecules were deposited by organic molecular beam deposition. The substrate reconstruction and ordering were checked by low energy electron diffraction. The molecular electronic, geometric structures and charge transfer properties were characterized by photoelectron spectroscopy, near edge X-ray absorption fine structure spectroscopy and resonant photoelectron spectroscopy (RPES). Scanning tunneling microscopy is used to directly image the molecular adsorption.

For phthalocyanines, we select MgPc, ZnPc, FePc and TiOPc, which showed a general charge transfer from molecule to the substrate when adsorbed on rutile TiO₂(110) surface with 1×1 and 1×2 reconstructions. This charge transfer can be prevented by modifying the TiO₂ surface with pyridine derivatives (4-tert-butyl pyridine (4TBP), 2,2'-bipyridine and 4,4'-bipyridine), and furthermore the energy level alignment at the interface is modified by the surface dipole established by the pyridine molecules. Annealing also plays an important role to control the molecular structure and change the electronic structure together with the charge transfer properties, shown by TiOPc film. Special discussions were done for 4TBP for its ability to shift the substrate band bending by healing the oxygen vacancies, which makes it an important additive in the DSSC electrolyte. For the triphenylamine-based dye (TPAC), the systematic deposition enables the characterization of the coverage dependent changes of molecular electronic and geometric structures. The light polarization dependent charge transfer was revealed by RPES. Furthermore, the iodine doped TPAC on TiO₂ were investigated to mimic the electrolyte/dye/TiO₂ interface in the real DSSC.

The whole work of this thesis aims to provide fundamental understanding of the interaction between photosensitive molecules on TiO₂ surfaces at molecular level in the monolayer region, e.g. the formation of interfacial states and the coverage dependent atomic and electronic structures, etc. We explored the potential of the application of new dyes and modified of the existing system by identifying their advantage and disadvantage. The results may benefit the fields of dye syntheses, catalysis researches and designs of organic photovoltaic devices.

Keywords: photoelectron spectroscopy, X-ray absorption spectroscopy, organic semiconductor, oxides, adsorption, dye sensitization, electronic structure, charge transfer
Acknowledgements

This thesis is not just a summary of my own work. It could not be accomplished without support from many people. First of all, I would like to express my deepest gratitude to my supervisor Doc. Mats Göthelid. You provided me this valuable opportunity to work in an extremely interesting field, surface science, which actually fulfills one of my high school dreams; I wished that one day I could see and touch atoms. I admire your sharp mind and benefit a lot (or feel a bit of pressure) from the thousands of interesting ideas constantly popping from your mind. You always trust me and encourage me to gain new knowledge and be brave when facing challenges. Whenever I need you, you are always available for a chat. In addition to scientific knowledge, I also learned to enjoy performing research from you. Your opera singing, whistling in the lab and corridor, and humorous jokes always warmed the working atmosphere while we were handling the cold vacuum chamber, which truly inspired me to progress with my own whistling. I feel very lucky to be your student.

I would like to express my sincere gratitude to Prof. Ulf Karlsson, my co-supervisor and the head of the research unit. Your valuable suggestions and help on my scientific research and general career development have greatly influenced me. Your opinions on daily life, especially regarding cross country skiing and soccer, always refresh me. In both China and Sweden, you and your wife Hua have given me great assistance.

My great gratitude to Prof. Oscar Tjernberg, the head of material physics, for interesting discussions on many scientific topics, some of which were very helpful throughout my studies and research. I would like to show my deep gratitude to Prof. Jan Linnros. Thanks for recruiting me as a master student in this department, which was instrumental to getting this PhD position.

Great thanks go to my colleagues from the surface physics group. I would like to thank the former group member Dr. Pål Palmgren for your strict training at the beginning of my PhD studies. Half a year of strict training made me feel safe and confident in front of different equipments through the four years to follow. I would like to thank Sareh Ahmadi for your indispensable help with all my experiments, especially at MAX-lab, the encouragement during different tough situations, and good advice on many things. I would like to thank Dr. Marcelo Zuleta for much support during experimentation and lots of interesting discussion of both science and society. I would like to thank Dr. Winnie Chow for your help in the lab and many interesting discussions about Hongkong and mainland. Your diligent work on the RHK STM has really impressed and encouraged me. Thank you to Dr. Anneli Önsten for being a perfect office mate and for frequent assistance in science and daily life, especially for an influential discussion when I was searching for my PhD position. I want to acknowledge Dr. Jonas Weissenrieder for your great help and useful suggestions on my research and career development. I have learned many things from your fruitful experience and kind attitude. Dr. Dunja Stoltz, thank you for constantly kind support and interesting discussions of many things. Our new group member, Markus Soldemo, I wish you a bright future.
Thanks to Dr. Chenghua Sun from the University of Queensland for the theoretical support and fun collaboration. Besides the collaboration, I also enjoyed many interesting discussions between us, and I miss playing the SanGuoSha card game with you. Thanks also to Dr. Haining Tian and Prof. Xichuan Yang for providing the TPAC molecule, which opened another door for my research. Dr. Qin Wang from Accero, thanks for the fun collaborations and interesting discussions.

I am very grateful to the present department administrator Madeleine Printzsköld. Thank you very much for constantly, kindly and patiently helping me with the whole preparation of my PhD disputation and many other detailed but important things. I would like also to show my gratitude to the previous administrator Marianne Widing for always being nice and supportive.

I would like to thank all the other previous and present members in the material physics division. Benjamin (a great office mate), Mahtab, Roody, Yashar, Aki, Torsten, Pooya, Milan, Dr. Martin Månsson, Dr. Thomas Claesson, Dr. Niklas Elfström, Dr. Ilya Sychugov, Dr. Karolina Szamota-Leandersson; “The Baltazar gang”: Magnus, Olof, Tobias, Bastian; the “Spintronics” group under Prof. Johan Åkerman, Sohrab, Majid, Johan Persson, Nadjib, Dr. Stefano Bonetti and all other new members. Thank you all for keeping the warm and positive environment in the department, which is one of the department attributes I love the most, and for your tolerance of my frequent disturbances during your work time.

Many thanks go to the MAX-lab staff: Dr. Franz Hennies, Dr. Annette Pietzsch and Dr. Karina Schulte for kind support at I511 and generously sharing your knowledge about photoelectron spectroscopy; Dr. Balasubramanian Thiagarajan, Dr. Mats Leandersson and Dr. Johan Adell for helping with the ARUPS at I4; Dr. Alexei Zakharov for helping me conduct the PEEM measurement. I am also very glad to know Chaofan Zhang, Dr. Xianjie Liu (LiU) and Dr. Zhuo Bao (now in USA) at MAX-lab.

I would like to thank Andreas Svahnström for solving all the computer problems. Thank my colleagues from other groups in KTH: Fei Ye, Yichen Zhao, Xiaodi Wang, Ying Ma, Dr. Shanghua Li, Dr. Jian Qin, Terrence, Dr. Jiantong Li, Si Chen, Dr. Yongbin Wang, Dr. Qing Lin, Dr. Jiajia Chen, Yiting Chen, Xi Chen, Vytautas, Zhiying Liu, and all the others for the diverse and interesting conversations.

Great thanks go to my friends (some are also colleagues): Kun Wang, Peng Zhao and their son; Guanqun Meng, Linlin Zhang and their daughter; Xingang Yu and Wen Yang; Andy Zhang and your family; Sha Tao and Jia Mao (Bangzi); Gang Wang, Yu Xiang, Jia Sun, and Chen Hu. Thanks to you, I have a colorful life in Sweden no matter if in summer or winter. I will always remember the happy times we spent together.

I would like to express my gratitude to my Kong Fu master Dr. Zhibin Zhang and your wife, Dr. Shiying Wu. You are good master and great friends. I learned not just Kong Fu technique from you, but more about life and research. My great American friend Thomas Liebmann, thank you for your miraculous patience of my English, sharing different ideas about lives and being a fantastic travel mate in China. Andrew Liebmann, the great tap dancer, and Pierre, the star of sports and music, thanks for many fun times with you.

Yeyu Fang, thank you for every moment we share and everything we have been through.
I would like to express my deepest appreciation of the friendship from my bros in China: Xiao Feng Yu, Ning Liu, Xuan Mark Zhang and your girlfriend Fan Zhang, Yong Andy Zhang and your wife Yi Yang, Zhipeng Zhang and your wife Yue Yu, Dr. Shoujun Wang and your wife Yingying Zhao (both now in USA), Kai Hu and your wife Qi Zhang (now in Japan), Zhao Li and your girlfriend Zhao Dong, Yijie Wang, and Yuan Yao (now in USA). Thank you for helping me solve different kinds of problems in China without any hesitation whenever I ask and for taking care of me, my colleagues and friends when in China; not to mention the countless memorable occasions when we hang out together.

I would like to thank Uncle Shide Yang, my father’s friend, for helping me with my presentation for IVC 18 conference. Thanks to you experience, I made a good performance in my first conference oral presentation.

I would also like to thank all my relatives for being supportive in these years. They are my grandparents, my auntie Min’s, Zhen’s, Baojin’s, and Baozhu’s families, my uncle Zhong’s, Hong’s and Baoqiang’s families. From daily trifles to life planning, I can always feel your care, understanding and encouragement in every aspect. Special thanks to my cousin Juan, her husband Gang and my cousin Lei for hosting me every time I stay in Beijing.

Last but not the least, my great gratitude to my mom and dad for your love and belief in me which has endowed me with endless power to approach my goals fearlessly. I feel so proud to be your son.
Publications

List of papers included in this thesis


III. Mats Göthelid, **Shun Yu**, Sareh Ahmadi, Chenghua Sun, Marcelo Zuleta, “Structure-Dependent 4-Tert-Butyl Pyridine-Induced Band Bending at TiO\(_2\) surfaces”, *International Journal of Photoenergy*, 2011, 110, 1–6


VIII. **Shun Yu**, Sareh Ahmadi, Pål Palmgren, Franz Hennies, Marcelo Zuleta, Mats Göthelid, “Adsorption of TiOPc on 1×1 and 1×2 reconstructed Rutile TiO\(_2\)(110) Surfaces”, in Manuscript
List of papers not included in this thesis


5. Xun Li, Qin Wang, Andy Z. Z. Zhang, Oscar Gustafsson, **Shun Yu**, Mats Göthelid, Susanne Almqvist, Amir Karim, Mattias Hammar, Jan Y. Andersson “Passivation and stability of InAs pin diodes embedded with type-II GaAs quantum dots” submitted to *IEEE Electronic Device Letters*, **2011**
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## Abbreviations

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<th>Abbreviation</th>
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<tbody>
<tr>
<td>2,2’-Bipy</td>
<td>2,2’-Bipyridine</td>
</tr>
<tr>
<td>4,4’-Bipy</td>
<td>4,4’-Bipyridine</td>
</tr>
<tr>
<td>4TBP</td>
<td>4-Ter-butyl Pyridine</td>
</tr>
<tr>
<td>AM</td>
<td>Air Mass</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction Band</td>
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<tr>
<td>CH</td>
<td>Core Hole</td>
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<td>CT</td>
<td>Charge Transfer</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>LEED</td>
<td>Low Energy Electron Diffraction</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>NEXAFS</td>
<td>Near Edge X-ray Absorption Fine Structure</td>
</tr>
<tr>
<td>OMBD</td>
<td>Organic Molecular Beam Deposition</td>
</tr>
<tr>
<td>Pc</td>
<td>Phthalocyanine</td>
</tr>
<tr>
<td>PES</td>
<td>Photoelectron Spectroscopy</td>
</tr>
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<td>RPES</td>
<td>Resonant Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>RT</td>
<td>Room Temperature</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
</tr>
<tr>
<td>STS</td>
<td>Scanning Tunneling Spectroscopy</td>
</tr>
<tr>
<td>TPA</td>
<td>Triphenylamine</td>
</tr>
<tr>
<td>TPAC</td>
<td>Triphenylamine–hydrophilic Cyanoacrylic acid dye</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultrahigh Vacuum</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra-violet</td>
</tr>
<tr>
<td>VB</td>
<td>Valence Band</td>
</tr>
<tr>
<td>VT</td>
<td>Variable Temperature</td>
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<tr>
<td>XAS</td>
<td>X-ray Absorption Spectroscopy</td>
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<td>XES</td>
<td>X-ray Emission Spectroscopy</td>
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<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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Chapter 1

Introduction

1.1. General background and motivation

$\text{TiO}_2$ is a wide band gap $\sim 3.0$ eV semiconductor (section 3.2). It has many applications\(^1\), for example, the band gap makes it a good absorber of the ultraviolet; in the painting and cosmetic industry $\text{TiO}_2$ is the white color pigment; for biological applications, it is a natural protection and biocompatible layer for the Ti bone implant material and can be used as antibacterial matter; in the electronic industry, it can be used as gate insulator in the microelectronic devices; in the architecture, it can be used as self-cleaning materials by using the superhydrophilicity, etc. Many applications actually stem from the important feature of the photoassisted catalysis of $\text{TiO}_2$, which is closely related to its surface properties.

The photocatalytical properties of $\text{TiO}_2$ was originally reported by Fujishima and Honda\(^2\) as the Honda-Fujishima effect: under UV illumination, water can be dissociated into oxygen and hydrogen gas at the $\text{TiO}_2$ surface, which has the potential to be a clean energy source and also to be used in the environmental protection. In the following periods, tremendous efforts have been put into the related fields in order to improve the efficiency. The improvements can be done in three ways by: i) doping $\text{TiO}_2$, ii) coating the $\text{TiO}_2$ surface with other metal clusters and iii) using photosensitive molecules or semiconductor particles to sensitize $\text{TiO}_2$ by adsorbing on the surface\(^3\).

The research work in this thesis focuses on the study of the photosensitive molecule/titanium dioxide ($\text{TiO}_2$) interface system for its important applications in catalysis and photovoltaic devices. Photosensitive molecules can also be called organic dyes or organic semiconductors with the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) comparable to the band gap of inorganic semiconductors. The adsorption of organic dye on the $\text{TiO}_2$ forms the so-called “dye sensitized $\text{TiO}_2$” systems, a typical organic/inorganic heterojunction. Dye molecules can absorb photons with longer wave length (lower energy) compared to $\text{TiO}_2$. Thus, larger portion of the solar spectrum can be used by the system. Under illumination, the electron will be excited from HOMO to LUMO, forming an exciton in the molecule. With a proper energy level alignment, the LUMO at the excited state can match with or be above the $\text{TiO}_2$ conduction band (CB) minimum. Consequently, the electron will be transferred to the $\text{TiO}_2$ substrate with a hole left in the molecule. Thus the electron/hole pair is separated at this interface. In the catalysis system, both the electron transferred to the substrate and the hole left in the oxidized molecule can be involved in catalyzing dissociation of adsorbents on the surface or materials in the electrolyte, for instance, dissociating water and degenerating the...
organic waste. In the case of dye sensitized solar cells (DSSCs), the electron injected into the TiO$_2$ substrate will be transported to the conductive electrode, such as indium doped SnO$_2$, and into the outer circuits. On the other side, the oxidized molecules are regenerated by the redox complex iodide (I$^-$/triiodide (I$_3^-$)) in the electrolyte which conducts the charge from the metal counter electrode$^4$. Compared to the traditional silicon based photovoltaic technique which requires advanced clean room laboratory and high cost, DSSC is made of cheaper materials and is easily fabricated.

Thus, understanding of TiO$_2$ surface and the interface between TiO$_2$ and other materials is of both scientific and technological importance. The surface and interface properties are usually different from that of the bulk structure and highly dependent on the surface orientation, atomic structure and electronic structure. In most cases, the device is made of TiO$_2$ nanoparticles to maximize the surface area such that the amount of dye adsorbed on the surface can be greatly increased. However, in the nanocrystals, many surfaces coexist and a large number and different types of defects can bring in the difficulties to specify the surface properties. Thus, the traditional surface science approach which is based on studies on single crystal under well controlled experimental conditions in ultrahigh vacuum (UHV) chamber is quite useful at this point. In surface science, several spectroscopy and diffraction characterization methods provide enough surface sensitivity by using different techniques, such as grazing incidence beam and capturing electrons with the minimum inelastic mean free path, etc (section 2.2 and 2.4). Meanwhile, the fast development of large synchrotron radiation facilities provide high performance light sources (section 2.1) which make the high resolution measurements easily accomplished. In this study, we combine different synchrotron radiation based spectroscopy with scanning tunneling microscopy (STM) which predominantly characterizes the surface electronic structure by using the tunneling electron (section 2.3). A sound knowledge of the characteristics of dye sensitized TiO$_2$ surface can be obtained.

Previously, a detailed review by Diebold$^1$ has summarized the scientific works on the surface properties of different single crystal TiO$_2$ surfaces, including the growth of metal layers and adsorption of inorganic molecules and simple organic molecules on the substrate. Based on this report, rutile TiO$_2$ (110) can be regarded as a model transition metal oxide surface. Because of its stable crystal structure and easy preparation, many experiments have been carried out on this surface, providing better understanding of surface structure and properties. The anatase TiO$_2$ nanocrystal is mostly used in the catalysis system for the higher efficiency. However, less is known about this metastable structure and the phase transformation from anatase to rutile will take place at high temperature thermal treatment depending on the impurities and sample history. Hence, in this work, most of the experiments were done on single crystal rutile (110).

Compared to the well studied adsorption system with metal and simple molecules, less known is the adsorption of large photosensitive molecules on the surface. There are many types of photosensitive molecules and the number of the new categories is increasing rapidly. In DSSCs, among the different dyes, ruthenium (Ru) complexes have been the research focus being the most stable and efficient dyes, some of which delivers the record efficiency about
11% under AM 1.5\(^1\) for nearly a decade\(^5\). By using different X-ray spectroscopy and STM, both organic ligands of Ru complex (e.g. bi-isonicotinic acid) and the entire molecules (N3, N719, etc) have been characterized\(^6\)-\(^{11}\). However, phthalocyanines and its analog porphyrins, which are widely used in the field of organic electronics and organic heterojunction solar cell\(^12\) owing to their good physical properties: the strong absorption coefficient in the visible and near IR region; long diffusion length of the charge carriers and high charge mobility; good thermal and chemical stability, etc\(^{13}\), usually yield a lower efficiency in DSSCs compared to the Ru complex. Recently, the porphyrin dye was determined to reach the 11% efficiency with the “push-pull” modification\(^{14}\). But for the phthalocyanine dye, the efficiency is still fairly low which is ascribed to the strong aggregation on the TiO\(_2\) surface rendered by the extend \(\pi\) orbital\(^{13}\). Researchers are trying to modify the phthalocyanines and porphyrins chemically for a better device performance. However, some fundamental questions of phthalocyanines/TiO\(_2\) interface\(^{15,18}\), such as the detailed bonding geometry, energy level alignment and charge transfer, still remain in spite of the vast number of studies of phthalocyanines/metal system. In this thesis, a large part of the work is the characterization of the interface between phthalocyanines (MgPc, ZnPc, FePc and TiOPc) and the single rutile TiO\(_2\). We first concentrate on the molecular adsorption geometry, energy level alignment and charge transfer properties on different surface reconstruction, and further use post-annealing and co-adsorption techniques to control and modify the adsorption of phthalocyanine on TiO\(_2\).

Besides the two families of dyes mentioned above, metal-free organic dyes are attracting more and more interest due to their higher molar extinction coefficients\(^1\), easier preparation and lower cost\(^{19,20}\). The recent record for metal-free organic dyes has reached around 10% (at 1.5 global sunlight, AM 1.5) provided by a triphenylamine and hydrophilic cyanoacrylic acid based electron donor–acceptor (D–A) structure dye\(^{21,22}\). To the best of our knowledge, the photoelectron spectroscopy characterization of triphenylamine−dyes/TiO\(_2\) has mainly been reported by Rensmo’s group\(^{23,24}\) on ex situ prepared dye molecules adsorbed on nanocrystalline TiO\(_2\), which provide fruitful information about the molecular electronic structure. For this type of dye, the packing mode of the dye influences the electron lifetime, which is believed to affect the open circuit potential\(^{25}\). Nevertheless, specific information on dye−dye interaction and adsorption geometry might be strongly influenced by residual solvents, impurities and irregular deposition due to the complex nature of the nanocrystalline substrate and the ex situ preparation. Hence, a characterization based on an in situ preparation which leads to a better controlled molecular deposition is of necessity and will benefit the further understanding of triphenylamine−based dyes\(^{25,29}\). In this part, we used the molecule, 2-Cyano-3-(4-N,N-diphenylaminophenyl)-trans-acrylic acid, which can be regarded as the simplest form of the triphenylamine-hydrophilic cyanoacrylic acid dye (section 3.1.2) and can be deposited by organic molecular beam deposition (OMBD) in UHV. Our study focuses on the coverage dependent molecular interaction including both electronic structure and molecular geometry change, and the charge transfer properties in the saturated thin film.

\(^{1}\) AM 1.5 or air mass of 1.5 refers to 1.5 atmosphere thickness, corresponds to a solar zenith angle of \(z=48.2^\circ\) with oxygen and nitrogen absorption\(^{17,18}\).

\(^{2}\) Molar extinction coefficient or molar absorption coefficient \(\varepsilon \ \text{(m}^2/\text{mol})\) is a measurement of how strongly a chemical species absorbs light at a given wavelength. It is an intrinsic property of the material and be described by the Beer-Lamber law: \(A = \varepsilon \cdot c \cdot \ell\) where, \(A\) is the actual absorbance of a sample; \(c\) is the concentration of the material and \(\ell\) is the pathlength.
Furthermore, the interaction between this dye and iodine was investigated in order to mimic the complicated TiO$_2$/dye/electrolyte “sandwich” interface.

Additionally, understanding the interaction between the TiO$_2$ surface and electrolyte species is another important issue in this thesis. For example, 4-$\text{tert}$-butyl pyridine (4TBP), one of the co-adsorbents in our research, is an important additive in the electrolyte of DSSC to improve the device performance. We have discussed the mechanism behind the 4TBP induced improvement on both rutile and anatase and determine the active site for 4TBP adsorption.

The whole work of this thesis aims to provide some fundamental understanding of the interaction between photosensitive molecules on TiO$_2$ surface, explore the potential of the application of new types of dyes and improve the existing system by identifying the advantages and disadvantages through the surface science approach. Even though it is just a beginning, we start to pave the path towards the ultimate goal to establish a model of dye sensitized surface at the molecular level.

1.2. Thesis structure

In chapter 2, the principles and equipments of experimental techniques are introduced including synchrotron radiation, different soft X-ray spectroscopies, scanning tunneling microscopy and low energy electron diffraction. In chapter 3, the detailed description on the molecules and substrates which have been used in the experiment are given. In chapter 4, the experimental results are presented and discussed. In chapter 5, the research works included in this thesis have been summarized and the prospective of the future studies are suggested. The included publications are attached in the appendix.
Chapter 2

Experimental methods

In this chapter, I will give a short introduction to the principles and equipments of different techniques. Surface and interface studies require well controlled experimental conditions. All experiments were completed in UHV with a base pressure around $1 \times 10^{-10}$ mbar and at room temperature. Both spectroscopy and microscopy have been employed as the characterization tools.

2.1. Synchrotron Radiation

Synchrotron radiation is a phenomenon that charged particles traveling the speed of light emit a highly collimated photon beam with the frequency spanning from IR to X-ray under acceleration. The first artificial synchrotron radiation was observed in 1947 and at present the main facilities are in the 3rd generation. However, the natural formation of synchrotron light exists since the birth of the Galaxy, by trapping charged particles in the magnetic field.

Modern synchrotron radiation facilities are constructed on the storage rings. A typical storage ring is a polygon connected by different straight vacuum pipes. The relativistic electron bunches are kept running along a defined path maintained by magnetic components in the storage ring. The whole ring is kept in UHV to minimize energy losses due to collisions between the electron beam and residual gas. By deflecting the electron bunches from one section to another, a strong photon beam is emitted along the trajectory of the path of electron bunches. Upon emitting light, electron bunches lose some energy. The lost energy will be compensated by accelerating the electron bunches in a radio frequency cavity.

The simplest device to deflect the electron is the bending magnet, a big pair of magnets. Today, in the 3rd generation synchrotron radiation facilities, insertion devices (wiggler and undulator) are commonly installed to further boost the brilliance. Figure 2.1 shows the trajectory of electron bunches in the three different devices and corresponding spectrum. Bending magnet is constructed simply by a pair of magnets, in which a homogeneous magnetic field is created. The moving electron will change direction under the Lorentz force. Since light is emitted along the trajectory of electron path, a light emission cone is formed in the bending magnet. The spectrum from a bending magnet is a continuum spectrum (Figure 2.1 (d)). For the insertion device, the structures of undulator and wiggler are rather similar: both of them consist of a periodic magnet array instead of a pair of magnets. But the wiggler has a much stronger magnetic field than the undulator. As a result, the wiggler spectrum resembles bending magnet’s spectrum but with much stronger intensity, larger divergence and higher energies (Figure 2.1 (e)), which is often used to generate the hard X-ray. To the

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*Brilliance = number of photons/(time × spot size × convergence × 0.1% band width)*
contrary, the weaker magnetic field of the undulator makes the light emitted in a smaller divergence than bending magnet and partially coherent (Figure 2.1 (f)) because the electron path is only diverged from the central position and the electron effective speed is almost close to the speed of light. As the photon generated by an undulator is partially coherent, interference of light from different magnets in the array make the photon intensity decline abruptly from the center photon energy. To maximize the intensity of the desired photon energy, the proper undulator gap between the two periodic magnet arrays should be adjusted.

![Figure 2.1 Schematics of electron trajectories in Bending Magnet (a), Wiggler (b) and Undulator (c); and the photon spectrum generated by bending magnet (d), Wiggler (e) and Undulator (f)](image)

All the light generated in the storage ring is conducted into the end-station through beamline equipped with the monochromator and focusing components. The experiments in this work are mainly completed at beamline I511 ($\nu$: 100 eV ~ 1500 eV) designed for UHV surface science research (now rebuilt into high pressure PES endstation) at the Max II ring and beamline I4 for high resolution angle resolve photoemission spectroscopy beamline ($\nu$: 13 eV ~ 200 eV) at the Max III ring, MAX-lab, Sweden.

The development of synchrotron radiation source has made it a scientific platform to perform versatile fundamental research like physics, chemistry and biology to applied technology e.g. materials science and information technology. The current advantages of synchrotron radiations can be summarized as: high brilliance, continuously tunable photon energy, broad spectrum, and controllable polarization. The ongoing development into the next generation e.g. free electron laser will further impel science and technology forwards.

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$^{\xi}$ The electron effective speed: the projected velocity on the central path.
2.2. Spectroscopy Techniques

In this work, different soft X-ray spectroscopy techniques have been used to probe the electronic structure and molecular geometry. In the following section, I will start from the general description of the principle of photo-electron interaction and then turn to a more detailed explanation of each specific spectroscopy.

2.2.1. Photon-electron interaction

![Figure 2.2 schematic of photon-electron interaction: (a) valence band photoemission spectroscopy; (b) X-ray photoelectron spectroscopy (XPS); (c) Auger-decay process after XPS; (d) X-ray absorption spectroscopy; (e) participator decay; (f) spectator decay and (g) Auger like decay due to charge transfer after the X-ray absorption process. Both (e) and (f) together are named as “autoionization”][1]

The photon-electron interaction here refers to the photoelectrical (Figure 2.2 (a) and (b)) and photoabsorption (Figure 2.2 (d)) processes as well as the subsequent events (Figure 2.2 (c) and (e)−(g)). The photoelectrical and photoabsorption are in principle the response of the electron in the material to the impinging electromagnetic wave and can be described by quantum mechanics using time dependent perturbation theory and semi-classical approximation. As a result, the transition probability \( w \) can be written in Fermi’s Golden rule as the following:

\[
\omega = \frac{2\pi}{\hbar} |\langle \Psi_f | \Delta | \Psi_i \rangle|^2 \delta(E_f - E_i - \hbar \omega)
\]  

(2.1)

Where, \( \Psi_f \) and \( \Psi_i \) represent the final and initial states of the N electrons system. \( \Delta \) is the perturbation operator. The \( \delta \) function guarantees the energy conservation. For a quantitative discussion, we can also use a simplified description for the observed spectrum by assigning initial and final state contribution. However, although this picture can explain many cases fairly well, the utilization of this picture should be under caution.

The fate of the hole generated by photoemission or photo absorption is to be refilled by an internal or external electron. For the valence band hole, the large amount of valence electrons can screen and refill the hole rapidly; for core holes, the recombination is usually in the form...
of fluorescence or Auger decays, namely the radioactive decay and non-radioactive decay. Auger decay is dominant for the core hole at the K-shell of low Z-atoms and L-shell of the atom with $Z < 90$\cite{12}. In this work, we focus on organic molecules which mainly consist of light weight atoms like C, N, and O. The recombination of their core hole is almost exclusively through Auger decay.

### 2.2.2. Photoelectron spectroscopy (PES)

The photoelectric effect was originally described by Einstein in 1905. Under illumination, the electrons in the materials can be excited into higher energy level by absorbing the photon energy. When the incident photon has sufficiently high energy, electrons can gain extra energy to break the material energy barrier (work function) and enter the continuum state (vacuum level). The whole process can be expressed as the following equation:

$$M + h\nu = M^+ + e^- \quad (2.2)$$

where, $M$ stands for the materials. By only observing the escaping electron, the energy conservation law is translated into:

$$K = h\nu - E_B - \phi \quad (2.3)$$

Where $K$ represents the electron kinetic energy, $E_B$ is the binding energy, $\phi$ is the work function (energy difference between Fermi level and vacuum level).

![Figure 2.3](image.jpg)

**Figure 2.3** The illustration of the photon energy dependent cross-section by measuring the frontier molecular orbitals of thick ZnPc film at 80 eV (dots) and 160 eV (voids) photon. The spectra were normalized to the intensity at the binding energy of 25 eV. The strong peak around 11 eV is the Zn3d orbital and the first peak around 1.5 eV is HOMO. Zn3d is greatly enhanced at by 160 eV while the organic orbitals have larger cross-section at 80 eV photon energy.

Historically, according to the incident photon energy, the photoelectron spectroscopy can be further classified as X-ray photoelectron spectroscopy (XPS or equivalently ESCA, Electron Spectroscopy for Chemical Analysis) and Ultraviolet photoelectron spectroscopy (UPS). However, at synchrotron radiation light sources, the distinction is rather vague since it is
possible to choose the photon energy continuously from UV to soft X-ray region. For this flexibility of selecting photon energy, one has to take into account of the photon-electron interaction cross section in order to select the appropriate photon energy for the measurement. Photon with different energy can excite the electron from the same orbital with different quantum efficiency. This becomes especially important for the valence band spectra. For example, Figure 2.3 shows that Zn3d and molecular orbitals have different photoionization cross-section at 80 eV and 160 eV. Yeh and Lindau\(^3\) have reported the full set of the cross section for 103 atoms at different photon energy. On a basis of this work, we can choose the proper photon energy to probe the molecular orbitals.

Figure 2.4 The “Universal Curve” of electron inelastic mean free path\(^3\). X-ray can penetrate deep into the substrate up to several microns; however, the photoelectron will experience inelastic scattering on the way out of the sample. We use the inelastic mean free path (IMFP) to characterize the average distance before photoelectron exchange energy with surrounding, e.g. collision with another electron. The IMFP is not only dependent on the material structure but also kinetic energy related namely “universal curve” \(^3\) (Figure 2.4). It shows that surface sensitivity will increase when the photoelectron kinetic energy is around 50 eV because the photoelectron from deeper substrate will be scattered and lose energy due to the smallest IMFP about 5 Å. In this work, we usually select the photo energy 50 eV higher than the core level energy to maximize the signal from the surface.

The surface sensitivity can also be used to determine the thickness of a thin film. The intensity from the substrate decreases exponentially with the increased thickness of upper layer, shown in Equation (2.4).

\[
I_d = I_0 \exp(-d / \lambda) \tag{2.4}
\]

Where \(I_0\) is the original intensity from depth \(d\) in the substrate, \(\lambda\) is the IMFP and \(I_d\) is the intensity collected at the surface. On the basis of the same principle, one can enhance the surface sensitivity by rotating the detector from normal emission angle to grazing emission angle. Then the photoelectron from deeper has a longer path to escape into the vacuum,
meaning larger chance to be inelastically scattered and lower intensity; the one from the surface area can however easily flee into the vacuum without energy loss, resulting in enhanced signal. (Figure 2.5)

![Diagram of normal emission and grazing emission](image)

\[ d = d' \cos \theta \]

Figure 2.5 The illustration of the normal emission and grazing emission.

The escaped photoelectron is collected by the photoelectron spectrometer. At present, the main design of a photoelectron spectrometer is constructed with retarding lens system connected to a concentric hemispherical analyzer (CHA) with double layer structure electrodes, and a micro-channel plate (MCP) detector at the end of the trajectory (Figure 2.6). The retarding lenses are used to adjust the incoming photoelectron to the same pass energy before they enter the hemispherical electrodes, where inner and outer shells are on different electrical potential and which conduct the electrons with only desired kinetic energy to the MCP detector, others with either higher or lower kinetic energy will collide with the electrodes. In the MCP detector, the signal will be enhanced owing to the cascade amplification of the number of electron. The large amount of electrons will hit a phosphorescence screen and a charge-coupled device (CCD) camera will record the intensity. By plotting this intensity per unit time versus the photoelectron kinetic energy (or translated binding energy), one can get the photoelectron spectra.

Interpretation and decipherment of the spectral characteristics can reveal physical processes and illustrate the material properties. The resolution of the spectra is limited by the external equipment resolution and also intrinsic core hole life time due to the uncertainty principle. The equipment limitation is related to the light source, optical component and the detector. Overall, it gives a Gaussian broadening to the spectra; the intrinsic life time broadening is Lorentzian shape profile. Thus, the final spectrum is a convolution of both Gaussian and Lorentzian and cure fitting is sometimes necessary to deconvolute the line profile into different components by using Voigt functions.

Before evaluating the spectral development, an energy reference point should be defined. For gas system, it is the ionization potential; for solid state system, the zero energy is usually chosen at the Fermi level. In our case, the Fermi level is measured from a metal sample clip which is made of tantalum in direct electrical contact with the TiO₂ substrate.
2.2 Spectroscopy Techniques

![Figure 2.6 the schematic of hemispherical analyzer.](image)

By XPS, we probe the core level electrons, i.e. in the inner shell of atoms, enabling element sensitive characterization. Meanwhile, core level binding energy reflects the chemical environment change by the chemical shift, which is one of the most important XPS applications. In a simplified picture, the chemical shift of a target atom is directly linked to the surrounding electron density. Larger charge density can shift the core level to lower binding energy while lower charge density shifts the core level to higher binding energy. The charge density is changed by the bonds to neighboring atoms: one with strong (low) electronegativity leans to attract (donate) electron, leaving lower (higher) charge density. To fit in the initial and final states pictures, the electron density induced binding energy difference is an initial state effect; whereas, after the photoelectron leaving the matter, the screening and electron refilling can be regarded as the final state effects. For molecular systems, the intensity of atoms with different charge density generally follows the molecular stoichiometry on account of the surface sensitivity.

In addition to determine the chemical states, XPS can also illustrate some other important spectra structures:

- Spin orbital splitting is commonly found for the sub shells (p, d, f... orbital) of the atom with the orbital angular momentum quantum number \( l \) larger than 0 (for s orbital, \( l=0 \)). Due to the spin-orbit interaction, the orbitally degenerated subshell will appear in the form of two separate peaks. The notation of the peak is as follows: element name + principal quantum number \( (n) \) + subshell orbital + total angular momentum quantum number \( (j) \), for example, Ti 2p\text{3/2} and Au 4f\text{7/2}, etc. In general, the energy splitting is regardless of the oxidation state, and the peak widths are basically the same for the same shell. However, given the events of fast intraband Auger decay (Coster–Kronig decay), the width of the spectrum can be largely broadened due to the shorter lifetime, such as Ti 2p\text{1/2} of TiO\text{2}\text{35}.

- Following the main characteristic line, some satellite peaks called shake-up and shake-off structures can also be found. They stem from the many-electron process when the outgoing photoelectron excites valence electrons into unoccupied states or
into the continuum state, thus the photoelectron will lose certain energy which correspond to interband transition or ionization energy. The final state of the material is thus at a different excited state with two holes in the system and one or no electron in the unoccupied orbital.

- Additionally, the characteristic Auger decay features with a constant kinetic energy are also collected by the spectrometer. Trouble might be introduced by carelessly choosing the impinging photon energy and the spectrometer energy window that the Auger peak superimposes with the core level structure, resulting in difficulties on the interpretation.

2.2.3. X-ray absorption spectroscopy (XAS)

When the incident photon has the exact energy equal to the excitation energy for elevating an electron from the core level into an empty state (unoccupied orbital for atoms and molecules and conduction band for solid) instead of exciting it into the vacuum level, the photon can be directly absorbed by the material without directly releasing an photoelectron. The measurement of this absorption coefficient as a function of the photon energy is X-ray absorption spectroscopy. Quantum mechanically, both XPS and XAS can be described by Fermi’s Golden rule, as mentioned in section 2.1.1. The two processes share the same initial state but the different final state. In XAS, the excited electron is populated into the unoccupied state, resulting in a fully self screened final state; in XPS, the photoelectron is in the continuum vacuum state. Thus, the relaxation of the ionized system is dependent on the surrounding electrical field and external transferred electrons. Meanwhile, XPS does not contain unoccupied state information, which is one of the important functions for XAS.

Since the measurement of X-ray absorption process requires a continuously tunable X-ray photon energy source, synchrotron radiation is the most suitable candidate. The photon energy can be tuned across the threshold, through the combined motion of monochromator and insertion device. Detection methods can be various from the equipment and research goals. It can be directly measured in transmission mode of comparing the photon flux before and after the sample. This benefits liquid research for the large penetration depth. However, since the penetration depth for solid materials is limited, it is more common for surface science to use Auger decay or fluorescence emission, stemming from the recombination of the core hole. The former is called electron yield detection; the latter fluorescence yield detection. The electron yield detection can be realized in different ways: total yield mode, partial yield mode and Auger yield mode. The total yield mode is performed by using XAS detector collecting all the electrons emitted from the sample including the characteristic Auger electrons, normal photoelectrons and inelastically scatter electrons, e.g. the secondary electron. Partial yield mode is the same as the total yield mode in principle but adding an additional retarding field to filter out the low energy electron and enhance the surface sensitivity. Auger yield mode is different from the above two. It requires the photoelectron spectrometer as a detector which can work with the energy window in a constant kinetic energy mode to collect the Auger electron. Thus the highest surface sensitivity can be achieved by Auger yield mode, which is also the detection method used in this study.

The absorption edge is generally related to the atomic subshell energy level, thus enabling the element sensitivity. By exciting electron from different subshell orbitals (s, p orbitals), the
process can be named as absorption at K, L−edge for the corresponding element, e.g. N K−edge absorption. The absorption spectrum shows a step-like line profile with an abrupt increasing at the absorption edge. By increasing the photon energy from the absorption edge to larger value, the whole spectrum can be divided into near edge X-ray absorption fine structure spectroscopy (0 ~ 40 eV) and extended X-ray absorption fine structure (up to several hundred eV).

During the measurement, the NEXAFS spectra are usually influenced by the quality of incoming light, for example, the light intensity may vary with the incident photon energy owing to the motion of monochromator and insertion device, and contamination, especially the C and Cr on the optic components equipped along the beamline. In order to properly separate the useful information from the background contribution, all the spectra have to be recalibrated. A normal way to calibrate the photo intensity is to place a gold mesh in front of the sample and record the photocurrent at corresponding photon energy during the measurement, and then normalize the absorption data points to the photocurrent at the same photon energy. To eliminate the contribution of contaminations along the beamline, especially for C K-edge measurement, a second normalization is necessary. The adsorbent’s spectrum has to be normalized to a spectrum which is taken from a well prepared clean sample. Furthermore, the photon energy should be calibrated for the measurement. Usually, it is done by measuring a core level by the first and second order light from the monochromator in the kinetic energy scale and comparing the energy difference.

![Diagram](image)

**Figure 2.7** the polarization dependence of NEXAFS spectra for $\pi^*$ and $\sigma^*$ orbital under $p$ polarization (a) and $s$ polarization (b)

From the molecular electronic structure, we know that the unoccupied orbitals are antibonding orbitals and $\pi^*$ to $\sigma^*$ orbital is aligned from low energy to high energy. For a molecule adsorbed on the substrate, the general NEXAFS spectrum looks like Figure 2.7. The first sharp peak or resonance represents the transition from the core level to the lowest unoccupied molecular orbital, usually $\pi^*$ orbital. The transition energy to $\pi^*$ orbital is lower than the ionization potential thus a trapped state. For the first resonance, it can be even smaller than the binding energy of the same core level determined by the photoemission measurement due to the strong Coulomb interaction between the core hole and the excited
electron. For the transition to $\sigma^*$ orbital which is above the ionization potential, the excited states are much less bound and the excited electron can be delocalized easily, resulting in a shorter lifetime for the excited state than that of transitions to $\pi^*$. In the spectrum, the $\sigma^*$ features appear much broader than $\pi^*$ features.

![Diagram](image)

**Figure 2.8** The schematics of the incident photon E vector and molecular orientation. $\Theta$ is the incident angle of photon. $\alpha$ is the normal vector of the molecular plane. $\phi$ is the azimuthal angle.

Photon absorption follows the dipole selection rule, which means that the relative angle between the photon polarization and orbital orientation can substantially influence the appearing peak intensity. In a simplified picture (Figure 2.7), the maximum transition intensity can be achieved in the complete overlapping between the photon polarization and the molecular orbital. Thus the molecular orientation of adsorbed molecules can be in principle determined by mapping the intensity as a function of the incident angle of the linearly polarized light. The intensities of the transitions to orthogonally oriented $\pi^*$ and $\sigma^*$ orbital are expected to vary conversely correspondingly. If ordered structures are formed on the surface and the substrate symmetry is considered, the molecular orientation can be further determined by the formula below according to Figure 2.8\(^2\):

- Substrate with two fold and higher symmetry, which is related to cosine of azimuth

$$ I_\nu \propto \cos^2 \theta \cos^2 \alpha + \sin^2 \theta \sin^2 \alpha \cos^2 \phi $$ (2.5)

- Substrate with three fold and higher symmetry, which is azimuth independent

$$ I_\nu \propto \frac{1}{3} \left( 1 + \frac{1}{2} \left( 3 \cos^2 \theta - 1 \right) \left( 3 \cos^2 \alpha - 1 \right) \right) $$ (2.6)

At least two different geometries are needed for three fold symmetric substrate and three geometries for two fold symmetric substrate, in order to determine the molecular orientation. Experimentally, we can use p and s polarization (Figure 2.7) with the grazing incident beam to fulfill the requirement on the geometry change instead of changing the incident angle. p polarization provide the E-vector normal to the substrate surface; s polarization means the E-vector is parallel to the substrate surface. Thus, two $\theta$ values are available. Additionally, the rotation of the sample orientation enables the adjustment of azimuthal angle for the two fold
2.2 Spectroscopy Techniques

symmetric substrate case. Inputting all the experimental parameters and spectral intensity, the molecular orientation problem is practically solvable.

2.2.4. Resonant photoelectron spectroscopy (RPES)

Resonant photoelectron spectroscopy can be regarded as a combination of XPS and NEXAFS. The measurement requires recording sequences of valence band spectra in either kinetic energy or binding energy scale at different photon energies consecutively tuned across a certain atom’s absorption edge. It is critical to understand the photo-electron interaction and distinguish different core hole decay processes (Figure 2.2) involved in the whole picture.

\[ P_{\text{NoCT}} = 1 - P_{\text{CT}} \]

No Charge Transfer

\[ P_{\text{CH}}^{\text{CT}} = 1 - P_{\text{CH}}^{\text{NoCT}} \]

(Autoionization)

Charge Transfer

\[ P_{\text{CH}} = \int_0^{t_2} P_{\text{CH}} \, dt_1 \]

\[ P_{\text{CH}}^{\text{NoCT}} = \int_0^{t_2} P_{\text{CH}}^{\text{NoCT}} \, dt_1 \]

(Core Hole Decay)

Figure 2.9 The schematics of the decay process of excitation state. \( P_{\text{CT}} \) and \( p_{\text{CT}} \) are the probability and density of probability of charge transfer at certain time \( (t_1) \); \( P_{\text{NoCT}} \) is the probability that charge transfer does not happen. \( P_{\text{CH}}^{\text{CT}} \) and \( p_{\text{CH}}^{\text{CT}} \) are the probability and density of probability of core hole decay at certain time \( (t_2) \). For the real measurement, the spectral signal is approximately equal to the case of \( t_2 \to \infty \), ended with a core hole decay. Without the charge transfer is the autoionization; with the charge transfer is the normal Auger decay.

In a simplified picture, below the absorption edge, all the photons interact with electrons in the fashion of the classic photoelectric effect, generating the photoelectron and delivering a normal photoelectron spectrum; Starting from the absorption edge, some of the photons are absorbed by the material due to the large absorption coefficient of the transition from the core level to the bound unoccupied orbital, while the rest is still involved in the normal photoemission process. For system at the resonant excited state, the autoionization process will occur to annihilate the core hole. Autoionization has two different decay modes\(^{31}\); participator decay and spectator decay (Figure 2.2 (e) and (f)). For participator decay, the excited electron will recombine with the core hole, releasing another electron from the valence band into the vacuum; for spectator decay, the excited electron will remain in the excited state and “witness” a normal Auger decay involving the recombination of one valence electron and the core hole and releasing the third valence electron into the continuum state. The decay channel usually involves the orbital from the same atom, thus the techniques has element sensitivity, revealing the contribution of different atoms to the valence band.
In an adsorption system where the molecule is bound to a solid substrate with a continuum energy level above the Fermi level, like metal or semiconductor, a possible charge transfer of the excited electron may occur from the adsorbate to the substrate. Consequently, the excited electron is no longer in the system. The annihilation of the core hole is completed through a normal Auger decay like the final state of photoemission process. Two valence holes will be left in the system thus a +2 ionization state, contrarily to one hole and a +1 ionization state created by autoionization. In this case, autoionization will thereby compete with the potential charge transfer process. Usually, the life time of core hole annihilated by autoionization is known and element specified regardless of the chemical environment, e.g. N1s 6 fs and C1s 7 fs. Thus, it is possible to estimate the charge transfer (CT) time for an adsorption system by distinguishing the normal Auger decay related features from autoionization decay signatures with the core hole (CH) lifetime as a time reference “clock”. This application is named as “core hole clock” method (Figure 2.9).

![Figure 2.10 The typical RPES image (take from ZnPc at N K-edge), the horizontal axis is photon energy and the vertical axis is binding energy](image)

In RPES, the resonant enhancement of the participator decay is always overlapping with the normal photoemission peak. From the energy point of view, the initial and final states are almost the same for the system compared to a normal valence band photoemission, and the emitted electron shows the same binding energy as a valence band electron. Contrarily, the normal Auger decay always shows a constant kinetic energy. For the spectator decay, it could also display as a constant kinetic energy feature when the excited intermediate state is coupled with a vibration mode and results in different screening conditions and/or that the photon bandwidth is larger than the lifetime broadening of the excited state. The spectator channel should show a shift to higher kinetic energy (called “spectator shift”) compared to the normal Auger channel due to the additional screening of from the remaining electron in the previously unoccupied orbital.

The appearance of autoionization enhancements indicate that the excited electron was not transferred away, while the normal Auger features mean the occurrence of the charge transfer.
This implicitly contains two issues which have to be taken into account before the utilization of core hole clock technique. The first one is whether the charge transfer is energetically allowed. Charge transfer only takes place when the excited state is overlapped with unoccupied conduction band of the substrate, which means energetically possible. However, in the X-ray absorption process, the first resonantly excited state sometimes falls below the Fermi level of the substrate due to the strong Coulomb interaction of the core hole and electron pair, which makes the charge transfer energetically unfavorable. In this case, the only way to annihilate the core hole is through autoionization. Hence, aligning NEXAFS and valence band spectra to the ionization potential in advance will be helpful to determine the excited states which are energetically available for the charge transfer. The second issue is a dynamic issue related to the charge transfer time. If the charge transfer time is too long compared to autoionization time, the autoionization feature will be dominant and normal Auger feature is barely visible, like at the charge transfer forbidden state. On the other hand, if the charge transfer time is too fast, then the autoionization will be largely quenched and no resonant enhancement can be seen except the strong Auger features. In these two extreme cases, the charge transfer time scale is beyond the detection limit which is generally defined as 0.1 to 100 fs.

RPES spectra are plotted as series of separate valence band spectra by manually tuning the incident photon energy across the absorption edge according to the NEXAFS spectra. In modern technique, the automatic synergetic operation of the photoelectron spectrometer and the monochromator largely facilitates the measurement with high quality image data and short experimental duration. For instance, the constant initial state (CIS) mode and constant final state (CFS) mode of Scienta spectrometer will fix the energy window in either constant binding energy or constant kinetic energy while adjusting the incident photon energy. The result is an image with photon energy and binding (kinetic) energy on two axes and the photoemission intensity as the third (Figure 2.10).

Based on the above description, the ideal tactic to analyze the data quantitatively is to extract the contribution of each decay channel. However, it is usually impractical owing to the complex superposition of different signals, which are not only from the different decay channels but also from valence band photoemission background. Thus, in order to properly determine the charge transfer time, both an isolated system and the coupled (charge transferred) system should be characterized by RPES and NEXAFS. The isolated system is used as a reference and normally represented by a thick film, in which no charge transfer is allowed by assuming no energetically available channel. The difference of the transition matrix between RPES and NEXAFS should also be taken into account and be calibrated by normalizing the intensity of the first resonant transition of RPES participator decay to that of NEXAFS. Then the charge transfer time ($\tau_{CT}$) can be calculated by comparing the $I_{\text{RPES}}/I_{\text{XAS}}$ difference between $iso$ and $CT$ system at the charge transfer state of LUMO + n (n=1, 2, 3...) and using core hole life time ($\tau_{CH}$) with Equation (2.7).

$$\tau_{CT} = \frac{(I_{\text{RPES}}/I_{\text{XAS}})_{CT} - (I_{\text{RPES}}/I_{\text{XAS}})_{iso}}{(I_{\text{RPES}}/I_{\text{XAS}})_{iso}} \cdot \tau_{CH} \quad (2.7)$$
2.3. Scanning Tunneling Microscopy (STM)

The scanning tunneling microscope can directly characterize the surface geometric and electronic structure, physical and chemical properties with very high resolution, which makes itself a very important tool in surface science and nanotechnology research. The prototype was invented by Gerd Binnig and Heinrich Rohrer (1981) at IBM in Zürich. In 1986, both of them were awarded the Nobel Prize for this contribution.

![Figure 2.11](image)

**Figure 2.11** The schematics of the empty state imaging (a) and occupied state imaging (b); $E_F$ and $E_{\text{Vac}}$ stand for the Fermi level (dashed lines) and the vacuum level (dot lines), respectively. Shadowed areas represent the occupied states (VB: valence band), while the blanked areas are the empty states (CB: conduction band). Under defined bias (+ or -), the electron tunnels into the empty states or from the occupied states of the substrate.

The principle of this microscope is fairly simple on a basis of quantum tunneling effect that electron can invade into the potential barriers which has higher energy than itself with a damping amplitude. The potential barrier can be created by vacuum, air or even liquid. Even though no direct contact exists, when the tip-substrate distance is within a few Ångstroms, the electron wave functions of tip and substrate can overlap. In this case, it is possible for the electron to tunnel through from either side to the other, resulting in a zero net current. By adding a small bias between the tip and a conductive substrate, a net current can be obtained. The tunneling current is found exponentially decaying with the tip-substrate distance $d$ and the square root of the bias ($E - E_F$) (Equation (2.8)), thus STM provide a very high vertical resolution typically around 0.01 Å. The lateral resolution of STM is governed by the tunneling current width, which is related to physical properties and electronic state of tip and sample surface. But to achieve an atomic resolution is not a problem for STM with a good tip on a flat conductive surface.

$$I \propto \exp\left(-2d \sqrt{\frac{2m(E - E_F)}{h}}\right) \quad (2.8)$$
By choosing the sign of bias from positive to negative, we can control the flowing direction of tunneling current. Figure 2.11 depicts the scenario between the energy level alignments with the current directions. When tunneling current flows from the substrate to the tip, electrons will fill into the unoccupied orbital of molecules and the conduction band of the substrate, providing information of the empty orbitals; when the current flows in the opposite direction, electrons from the occupied orbital of the molecule and the valence band of the substrate go to the tip, which delivers information of the filled orbital. Thus selecting different bias will enable us to see spatial distribution of the electronic structure on the surface. Derived from this concept, scanning tunneling spectroscopy (STS) can be used to characterize the spatial distribution of the energy level by measuring $I/V$ curve at each single measuring point and plotting the $(dI/dV)/(I/V)$ signal.

The general design of a STM system is illustrated in Figure 2.12. Before scanning, the coarse motion will bring the tip towards the surface until the tip-substrate distance is within the tunneling region and a stable tunneling condition is achieved, which is decided by the preset bias and reference tunneling current. The atomically sharp metal tip usually made of tungsten or platinum-iridium alloy is controlled by several peizo components (i.e. X, Y and Z) so that the tip can move freely along three directions. X and Y components will move the tip line-by-line to map the whole surface. The Z component controlled movement is dependent on the selected scanning mode: constant current mode or constant height mode. The tunneling current under the set bias will be converted into a voltage signal through the preamplifier and transferred to the control unit. If constant current mode is used, this signal will be compared with the setpoint in the feedback loop. In case of deviation, the control unit will send a signal to the Z component to adjust the tip-sample distance till the tunneling current back to the setpoint value. The corresponding movement of the Z component mirrors the surface topography, which will be recorded and plotted into the image. If constant height mode is chosen, the feedback loop is then deactivated. The surface topographic variation will directly cause the alternation of the tunneling current, which can be translated into geometric information by the control unit of a calibrated system. Directly plotting this translated
information will also deliver a topographic image. However, an activated feedback system can protect the tip from potentially crashing into the surface, especially when the surface roughness is large. Thus, constant current mode is normally used.

In order to display the fine structure at atomic level, the whole STM system requires a good damping system. Human voice, building vibration or any sudden perturbation by jumping on the floor and touching the system could cause the loss of a stable tunneling state. Especially for UHV STM, the system is kept in a UHV chamber with some built-in noise source, e.g. turbo and roughing pumps. In general, the system is kept underground and using heavy concrete fundament which is isolated from surrounding floor or damping legs as support in order to damp building and sound vibration. A second stage damping system is needed for the STM measuring stage. For Omicron VT STM, the whole measurement stage is suspended by four springs and with an eddy-current damping system to further reduce disturbance. For the image processing, the software WxSM is used. Besides the necessary equipments and software, the operator should be patient and consistent during the measurement, which sometimes is more important.

2.4. Low Energy Electron Diffraction (LEED)

The surface structure sometimes has different construction compared to that deduced from the truncate bulk. Relaxation and reconstruction may alter the unit cell parameter and introduce some new structures to lower the total energy. Besides directly measuring the surface structure by STM, we also use diffraction techniques to determine the ordered surface structure, as characterizing the bulk crystal structure. However, different from the bulk structure characterization, the weak surface signal should be enhanced by the techniques with higher surface sensitivity. The low energy electron (typically 20 – 200 eV) cannot penetrate deep into the substrate for the strong interaction induced short IMFP. Thus, only the elastic back scattered signal from the surface follows the diffraction rule forming diffraction pattern. This technique is called low energy electron diffraction. It is also possible to use high energy electron but in the reflection mode instead of back scattered mode, which is usually called Reflection high energy electron diffraction (RHEED). In this work, only LEED has been used.

To precisely describe the principle of LEED, a complicated dynamic theory considering multi scattering process is needed. However, to simply use LEED to check the surface cleanness and ordering in a macro scale as in this work, the kinematic theory description based on single scattering is sufficient. In this theory, the electron beam will be represented by a plane wave with the de Broglie wavelength $\lambda$. The diffraction follows Bragg’s diffraction law by given the normal incident electron beam and the angle between surface normal and detector:

$$n\lambda = d \sin \phi$$  \hspace{1cm} (2.9)

Where, $d$ is surface unit length.

During the elastic diffraction both energy and momentum are conserved, and only the direction of momentum is changed. Thus, the whole LEED process can also be described by Laue condition using the 2-D reciprocal space and Ewald Sphere. The way to construct a 2-D reciprocal space is following Equation (2.10).
2.4 Low Energy Electron Diffraction (LEED)

\[
\begin{align*}
\mathbf{a}^* &= 2\pi \cdot \frac{\mathbf{b} \times \mathbf{n}}{\mathbf{a} \times \mathbf{b}} \\
\mathbf{b}^* &= 2\pi \cdot \frac{\mathbf{n} \times \mathbf{a}}{\mathbf{a} \times \mathbf{b}}
\end{align*}
\]  

Where, \( \mathbf{a} \) and \( \mathbf{b} \) are the surface lattice constant while \( \mathbf{a}^* \) and \( \mathbf{b}^* \) are the reciprocal lattice constant. \( \mathbf{n} \) is a unit vector normal to the surface plane. The difference between 2-D and 3-D reciprocal spaces is that the third dimensional points can be replaced by a rod which is perpendicular to the 2-D reciprocal plane. The Ewald Sphere is a reciprocal sphere with incident electron wave vector as the radius. Since the incident beam is ideally normal to sample surface, 2-D reciprocal plane is the tangent plane of Ewald Sphere with the contact at (0,0). The intersect points of Ewald Sphere with the reciprocal rods geometrically fulfill the Laue condition (Figure 2.12).

Figure 2.13 In the left, the schematics of the translation between the real space and reciprocal space; in the right, the illustration of Laue condition by Ewald sphere and surface reciprocal pattern. \( \mathbf{K} \) and \( \mathbf{K}' \) are the wave vectors of the incident electron and the elastically scattered electron. \( \mathbf{K} \) is perpendicular to the surface reciprocal lattice. \( \mathbf{G} \) is a vector between the surface reciprocal columns. \( \mathbf{K}, \mathbf{K}' \) and \( \mathbf{G} \) follows \( \mathbf{K}'=\mathbf{K}+\mathbf{G} \) because of the momentum conservation law.

Experimentally, the LEED setup is constructed in such a way that a monochromatic electron gun is equipped in the center of the spherical detector screen with three or four layers of grid electrodes. The electron gun can provide an adjustable electron beam with the beam diameter about 1 mm and the typical energy range from 10 to several hundred eV. The first layer grid of the detector is grounded to form a field free space above the sample surface. The second and the third grids are used as the filter to block the inelastically scattered electron with low energy. The fourth layer is also grounded to protect the filtering field created by the two
layers in front from the final screen, which is on a high bias to accelerate the filtered electron beam such that they can have enough energy to make phosphor coating glow.

![Figure 2.14 The schematics of LEED construction](image_url)

Figure 2.14 The schematics of LEED construction

The sharpness and the shape of the diffraction spots of LEED are related to the orderings of the surface. Perfect surface arrangement and large terraces usually render sharp and small diffraction spots with high contrast and low background. Insensitive to single impurities and defects, LEED pattern can otherwise be weakened and blurred by amorphously distributed large amount of defects and impurities. Furthermore, the small terraces will create additional diffraction between the layers at different heights in the direction normal to the surface. As a result, the reciprocal space is not a perfect rod but modulated by extra structure, which will also contribute to the spot shape. For instance, an extreme and special case is the vicinal surface, on which the quasiperiodic distributed surface facets form a reciprocal space tilted with certain angle to the main surface, resulting in extra spots in the LEED pattern around the main ones. Even more complicated analysis regarding the diffraction intensity requires dynamical theory, which is beyond the application of LEED in this work, thus not included here.
Chapter 3

Materials

In this chapter, the materials involved in this research are introduced. For a normal adsorption study, it requires the participation of adsorbents and the substrates. In this project, the adsorbents are different organic molecules: phthalocyanines, triphenylamine-based dye and pyridine derivatives. The former two are photosensitive molecules which play a role to sensitize the substrate; the latter are used as co-adsorbent to modify the substrate surface properties and adjust the molecular interaction. For the substrate, most of the experiments were completed on the single crystal TiO$_2$ rutile (110) surface and some were done on single crystal TiO$_2$ anatase (100) surface.

3.1. Molecules

3.1.1. Metal-Phthalocyanines

Phthalocyanine is a macrocyclic organic molecule (Figure 3.1 (a)) using four bridging nitrogen atoms to link four lobes which are structured as a pyrrole ring connected to a benzene ring with a shared C-C bond. The first phthalocyanine was synthesized accidentally by Braun and Tcherniac in 1907 and the structure was not fully understood until 1933 by Prof. Linstead and his students.$^{43}$

![Figure 3.1 The molecular structure of metal-free phthalocyanine (a) and metal phthalocyanine (b); M represents metal and replace the two hydrogen atoms in the metal-free phthalocyanine.](image)

Phthalocyanine has a famous chemical flexibility such that the two hydrogen atoms can be replaced by metal atoms, oxo-metal or halogen-metal moieties from every group of the periodic table forming metal-phthalocyanine (Figure 3.1 (b)). With the introduction of the metal orbital, especially the d orbital, molecular frontier orbitals, e.g. HOMO and LUMO, can
be modified. The metal center can interact with substrate in form of coordinator bond, inducing different adsorption modes. Phthalocyanine is also good platform to synthesis different organic derivatives. For example, the hydrogen atom can be replaced by different halogen atoms. Furthermore, the periphery can be linked to different ligands, which also modifies the molecular interaction, packing mode and physical properties. Many studies have been carried out about the modification at the periphery. In this work, we shall put our focus on the discussion of the influence of the center metal to the phthalocyanine and try to generalize the phenomena during adsorption.

Traditionally, phthalocyanines are widely used as green and blue color pigments in the dye industries. With an impressive thermal and chemical stability, the phthalocyanine can survive the temperature of 500°C. With the advancing development of organic based devices, such as Solar cell\textsuperscript{12} and OFET\textsuperscript{44}, phthalocyanines have become one of the main organic materials for the device fabrication.

![Figure 3.2 In the left, the nomination of the atoms in the example of zinc phthalocyanine (ZnPc): Carbon atoms are in dark grey; hydrogen atoms are in light grey; nitrogen atoms are in blue; Zinc atom is in green. Benzene carbons (C\textsubscript{B}, within red circle), Pyrrole carbons (C\textsubscript{P}, within green circle), three coordinated nitrogen (N\textsubscript{3c}, blue solid circle) and two coordinated nitrogen (N\textsubscript{2c}, blue dashed circle) are marked along one lobe. The rest carbon and nitrogen atoms can be classified into the four groups according to the symmetry. In the right the distributions of frontier orbitals of ZnPc are illustrated.](image)

The semiconductivity is regarded as an intrinsic property of phthalocyanine. The molecular structure renders phthalocyanine an aromatic electronic structure. For most of the metal-phthalocyanine the main absorption wavelength in the visible region lies between 600 to 700 nm, close to that of metal-free one. It is often assigned to the transition between HOMO and LUMO. The organic frontier orbitals of different phthalocyanienes share almost the same orbital distribution. The organic ligand $\pi$ ($a_{1g}$) and $\pi^*$ ($2e_g$) orbital\textsuperscript{††} are the HOMO and LUMO, for example ZnPc (Figure 3.2). Some exceptions, such as FePc and CoPc, have the metal d orbital as the HOMO. The bond between metal center and four surrounding nitrogen atoms can be either covalent or electrovalent\textsuperscript{45}.

\textsuperscript{††} u and g stands for ungerade and gerade, or asymmetry and symmetry of a center of inversion.
In general, the molecular structures of metal phthalocyanines can be roughly classified into two groups: planar structure and nonplanar structure. H$_2$Pc and most of MPc planar structure, with the exception of Lead and Tin, the radius of which are too large to be incorporated into the organic ligands. For the nonplanar structure, a detailed summary has been made by Michael Engel.

MgPc and ZnPc are quite alike in the molecular structure with a long metal nitrogen bond length around 2.010±0.002 Å according to a theoretical simulation of the ground state. They also resemble each other in the electronic structure with the HOMO and LUMO contributed by the organic ligand. This is probably because the Zn atom has fully filled d orbital hidden deeply below the organic frontier orbital, which makes Zn$^{2+}$ and Mg$^{2+}$ similar since all the subshell are filled. For FePc, the molecular HOMO is mainly contributed by Fe d orbital instead of organic ligand as well as part of LUMO. The open d shell orbital enables many possibilities to tune the molecular properties through modification of the electron spin at the iron center by either substrate and/or external ligands, like amine, pyridine, and carbon monoxide. “Iron, magnesium, and zinc atoms, after entering the phthalocyanine ring, do not completely lose their ability to react with electron donors.”

TiOPc has a titanyl group (Ti=O) integrated in the center of organic ligand with a Ti atom bound to the inner nitrogen (Figure 3.5). The electronic structure has been characterized by Zhang et al. using XPS and XES. TiOPc has C$_{4v}$ symmetry and shuttle-shape geometry, which renders convex and concave structure in the condense phase. The packing modes of the TiOPc are mainly found in four different types: amorphous, α–phase (phase II), β–phase (phase I), γ–phase (phase Y). By controlling the deposition rate and the substrate temperature, one can manipulate the crystal structure from amorphous to a mixture of the crystalline Phase I and Phase II in UHV. The latter is more favored on crystalline substrates and at higher temperature treatment. Photoelectron spectroscopy (PES) and X-ray emission spectroscopy have been used to characterize the intrinsic electronic properties of crystallized TiOPc, the effect of atmospheric doping, and TiOPc/C$_{60}$ donor-acceptor dimers, etc. Discussions on intramolecular and intermolecular charge transfer, such as the Ti-N and Ti-O charge transfer, can also be found in such investigations based on resonant inelastic X-ray scattering (RIXS) at the Ti L-edge.
3.1.2. Triphenylamine–hydrophilic Cyanoacrylic acid

Electron donor-acceptor complex, also called charge-transfer complex, is a type of molecular entities or a single molecule in which a constant electrostatic force is built up between the electron donor, from which the electron is transferred out (HOMO) and the electron acceptor, to which the electron hops (LUMO). Under illumination, the electron from HOMO will directly be excited into the spatially separated LUMO. Thus, electron donor-acceptor complexes facilitate the charge separation, which benefits the solar cell efficiency. Commonly used donor-acceptor dyes in the dye sensitized solar cell are ruthenium complexes. However, the scarcity of ruthenium and the drawbacks of transition metal for the environmental pollution encourage the researchers to search new pure organic dye. Triphenylamine-based dyes are one of the competitors, one of which has delivered 10% efficiency under 1.5 AM (solar spectrum)\(^2\). This is an output close to the around 11% record created by the “black dye”, a ruthenium complex, for nearly a decade\(^5,59\). The triphenylamine-based dyes consist of three parts: donor, linker and acceptor\(^6\). The design strategy has been discussed on a basis of computational investigation\(^61\).

Triphenylamine is an organic structure with a nitrogen atom linked to three phenyl groups\(^62\). Different from most of the amines, Triphenylamine is nonbasic. Electrons are distributed perpendicular the plane defined by NC\(_3\) single bonds in form of sp\(^2\)- or sp\(^3\)- hybridization. The three phenyl group is rotated around the N-C bond about 41.75\(^\circ\)\(^63\). Triphenylamine derivatives are commonly used as hole conductor in organic photoelectronic devices\(^64\). In donor-acceptor complex, it is the electron donor.

The linker usually possesses a \(\pi\) orbital system varying from C=C double bond to aromatic group\(^25,26,29\) to conduct the excited charge from the donor to acceptor. The elongation of the linker group can shrink the energy gap between HOMO-LUMO\(^29,65\) and induce a change of packing mode on the TiO\(_2\) surface\(^24\), which further influence the open circuit voltage\(^25\).

The acceptor behaves like an “electron pump”. Like the linker, there are different anchor groups. Wiberg et al.\(^66\) have pointed out that a cyanoacrylic part is a good electron attractor owing to injecting the electron further into the TiO\(_2\) nanoparticles, which prevents the recombination of the electron-hole and results in a high efficiency for D5 dye, whereas, the rhodanine anchor group only injects the electron on to the surface of TiO\(_2\), causing an easy recombination of electron at the surface trap state.

The molecule requires the anchor group to form a firm attachment to the substrate. The anchor group is almost always carboxylic acid. Upon adsorption on the TiO\(_2\) surface, hydrogen atom will break from the carboxylic group and the whole group will bond to the 5 fold coordinated surface Ti atom in form of carbonate through the two oxygen atoms, like HCOOH\(^1\), bi-isonicotinic acid\(^67\), and different amino acids\(^68\).

In this work, we used the synthesized triphenylamine-hydrophilic cyanoacrylic acid (2-Cyano-3-(4-N,N-diphenylaminophenyl)-trans-acrylic acid) by our coworkers Dr. Haining Tian and Prof. Xichuan Yang, according to a published procedure\(^69\). The molecule itself can be regarded as almost the simplest form of triphenylamine-based dye. TGA and DSC data shows that no strong dissociation and phase transition occurs under 150\(^\circ\)C. The molecule was thoroughly outgassed at around 100\(^\circ\)C for more than 72 hours in UHV till no impurities,
mainly water, were detected before experiment and was evaporated at 130°C during deposition in UHV.

Figure 3.4 TPAC dye powder (up) and molecular structure (down) which is divided into three parts: TPA, Tail and Anchor groups.

3.1.3. Pyridine derivatives (Pyridinyl)

Pyridine (C5H5N) is a heterocyclic organic compound with similar structure as benzene with one C–H group replaced by a nitrogen atom. The numbering of the atoms in the pyridine ring and its schematic of electron structure are shown below (Figure 3.5). It is an aromatic molecule with 6 conjugated π electron delocalized along the molecular ring. The lone pair electrons of the nitrogen atom are oriented within the molecular plane and protruding outwards. Thus the whole molecule displays a weak Lewis base property.\textsuperscript{70} It can then be used as a probe to identify the acid reaction site of oxides\textsuperscript{70} or modify the transition metal.

\textsuperscript{70} In chemistry, if the electron donor can provide a pair of electrons instead of a single electron the molecule is then called Lewis base.
catalysis. By connecting different ligands to the pyridine ring, we can get versatile pyridine derivatives, all of which together are called pyridinyl.

- **4-tert-butyln pyridine (4TBP)**

By replacing a hydrogen atom with a tert-butyl group \([–C(CH_3)_3]\) at position 4, one gets 4-tert-butyln pyridine, a colorless liquid with strong smell. Lacking of diffraction experiment, the structure of the 4TBP is assumedly better described by DFT (B3LYP/6-31G) by comparing different simulation results (BLYP and Hartree-Fock) and experimental data of pyridine. A schematic structure of 4TBP is shown in Figure 3.6. The tert-butyl is believed to generate an inductive effect (+I effect) on the aromatic ring, leading to a higher charge density around the nitrogen atom.

![Schematic structure of 4TBP](Image)

**Figure 3.6 Chemical formula (left) and 3-D illustration of molecular structure of 4TBP; Carbon atoms are in cyan; nitrogen is in blue; hydrogen atoms are in white.**

4TBP is an important additive in the electrolyte of DSSC. Already in 1993, it was discovered through I-V measurements that the addition of 4-terbutyl pyridine (4TBP) to the \((I_3/I^-)\) electrolyte increases the fill factor and the open circuit voltage \((V_{oc})\) approximately by 0.4 eV, without affecting the short circuit current of the cell. This is ascribed to 4TBP occupying active sites on the TiO₂ surface. Later, Schlichthörl et al. suggested based on the results obtained from intensity modulated photovoltage spectroscopy that the main reason for the increase in \(V_{oc}\) stems from a 4TBP-induced shift of the TiO₂ conduction band edge towards lower binding energies. On the other hand, Nakade et al. and Boschloo et al. proved that 4TBP adsorption can reduce the concentration of adsorbed protons, Li⁺ and/or other cations from the electrolyte to the TiO₂ surface. It was suggested that the band shift exerted by cations is in opposite direction to that caused by 4TBP, i.e. towards higher binding energies. Furthermore, 4TBP also decreases the electron recombination from TiO₂ to tri-iodide present in the electrolyte, by blocking the transport of tri-iodide to the surface or, at the same time, by removing adsorbed iodine from the surface.

---

\[\text{An experimentally observable effect (on rates of reaction, etc.) of the transmission of charge through a chain of atoms by electrostatic induction}\]

The effects induced by the added electronegative atoms and groups which release or withdraw the electron from the organic entity are called +I effect or –I effect, respectively. Correspondingly, the atoms or groups are named as +I group or –I group.
• 2,2′-bipyridine and 4,4′-bipyridine

![Chemical structures of cis and trans 2,2′-bipyridine](image)

**Figure 3.7** The chemical formula of 2,2′-bipyridine in *cis* (a) and *trans* (b) structures.

2,2′-Bipy is formed by linking two pyridine ring at position 2. It is the main component of metal complex. For example, in the DSSC industry, the efficient ruthenium complex mainly consists of Bi-isonicotinic acid (2,2′-Bipy with two carboxylic group). In the nature, it has two natural forms: *trans* and *cis*, which have been investigated by spectroscopy and theoretical calculation. The *trans* isomer is commonly found in a planar structure in gas phase, crystal or a approximately planar structure in nearly all solvents. Upon adsorption to metal or mineral surfaces, a transfer from *trans* to *cis* may occur owing to the coordination center on the substrate surface to form metal complex. The optimum rotation angle between the two pyridine rings of *cis* conformer is around 44.9° with the barriers of *trans/cis* interconversion about 5.6 kJ·mol⁻¹ according to calculations.

![Chemical formula and 3-D illustration of 4,4′-bipyridine](image)

**Figure 3.8** The chemical formula (up) and 3-D illustration of the molecular structure (down) of 4,4′-Bipyrene. Carbon atoms are in cyan; nitrogen atoms are in blue; hydrogen atoms are in white.

4,4′-Bipy consists of two pyridine ring linked through the position 4 by a single bond. The two rings are twisted from each other at an angle around 40°, where the torsional potential reaches the minimum. 4,4′-Bipy is commonly used as the linker in the metal-organic complex and as the prototype of single-molecule junction for the molecular electronic devices. Upon adsorption of 4,4′-Bipy on metal surface in electrolyte, the nitrogen atom is usually coordinated to the substrate atoms with some self-assembled structure. The adsorption geometry is found to be related to the potential on a Au electrode. Theoretical calculations show that for 4,4′-Bipy adsorbing on the alumina surface, the pyridine ring unattached to the surface does not suffer from geometrical and vibrational change.
3.2. The Titanium Dioxide Substrate

Titanium dioxide is a wide band gap semiconductor, with an energy gap about 3.0 eV. It, especially in the form of nanostructured crystal, has many applications spanning over several fields: catalysis, microelectronics, gas sensors, protecting layers, etc. It has three main natural crystal structures: rutile, anatase and brookite. Among them, the rutile structure is the most common format for TiO$_2$, followed by anatase and least brookite$^{95}$. Both rutile and anatase attract much research interest for their application in the field of energy conversion and photoassisted heterogeneous catalysis and both of them are well studied by surface science techniques. The anatase phase can transform into the rutile phase at high temperature, depending on impurities, sample size and sample history.

For natural crystal, the intrinsic impurities (oxygen vacancies and Ti interstitial atoms) give the bulk a dark color; while pure crystals are transparent. However, TiO$_2$ can easily be reduced and consequently, the sample color will vary from the transparent to light and finally to dark blue, corresponding to the extent of reduction. By artificially increasing those intrinsic defects through heat treatment in UHV, the sample conductivity will be improved, avoiding the sample charging in the PES and LEED measurement and fulfilling the requirement of STM measurement. As a result, TiO$_2$ becomes an n-type semiconductor. Below, I shall give a short introduction about experimental substrate rutile(110) and anatase(100). A more detailed description of surface science research on TiO$_2$ can be found in the review article written by Ulrike Diebold$^{95}$.

3.2.1. Rutile (110)

The rutile crystal structure has a tetragonal lattice with unit cell parameters a=4.584Å and c=2.953Å; each Ti atom is coordinated to six oxygen atoms; while each oxygen atom is coordinated to three Ti atoms, which forms the octahedral building blocks of the crystals. The (110) surface is the most stable surface with the lowest surface energy according to theoretical calculation. The bulk truncated (110) is terminated with 5 fold coordinated Ti atoms in rows along [001] connected to 3 fold coordinated oxygen atoms and alternating 2 fold bridging oxygen rows, below which is 6 fold coordinated Ti atoms. Qualitatively, the surface is described as a nonpolar and autocompensated surface$^{95}$ by combined pure electrostatic consideration$^{96}$ and autocompensation concept$^{97}$ owing to 1.) The surface is charge neutral and 2.) The same amount of Ti→O and O→Ti bond was broken when the structure was created.

The rutile (110) 1x1 surface structure resembles the bulk with the same lateral size of surface unit as the bulk unit in that the in-plane relaxation is symmetric to 5 fold coordinated Ti rows. The main relaxation is perpendicular to the surface, resulting in a slightly wrinkled surface. When the substrate becomes heavily reduced by high temperature for a long period, a 1x2 reconstruction may appear on the surface, usually initially growing along the [001] from the terrace edge. Historically, three models of 1x2 have been proposed: missing row$^{98}$, added row and added “Ti$_2$O$_3$” row$^{99}$. The latter two models are advocated by the experiments and theoretical calculations$^{99}$. For 1x2 LEED pattern, additional spots appear in the middle of 1x1 spots along the [-110] (Figure 3.9). The sample contains natural impurities like Ca and K, as well. During sample preparation, these impurities can diffuse from the bulk to the surface,
forming some compounds which shows different LEED pattern. Thus, cycles of sputtering and annealing are required to clean the surface.

![Figure 3.9 rutile TiO$_2$(110) 1×1 (a, 100.0 × 100.0 nm$^2$) and 1×2 (b, 70.0 × 70.0 nm$^2$) reconstructions, the upper inserts are LEED pattern for 1×1 and 1×2 dominant surface; the lower insert (a) is rutile unit cell, in which the yellows are Titanium atoms and the reds are oxygen atoms. In (a), [001] orientation is marked by the arrow; in (b), the double 1×2 strands are aligned with [001] orientation.](image)

For STM measurement of rutile (110) 1×1, only successful achievements were reported from the n-type substrate under positive bias, which means that the tunneling electron flows from the tip to substrate conduction band$^{100}$. Thus, STM interpretation of TiO$_2$ is a tricky issue and under debate in the past for two competing factors: 1) 5 fold coordinated Ti atoms dominate the conduction band minimum, and 2) bridge oxygen atoms are protruding out from the surface, thus dominating the geometric structure. The theoretical calculation shows that the 5 fold coordinated Ti atoms are dominant for the CB in a large distance, thus it is possible for Ti atoms to be imaged as a bright protruding structure by a “clean” tip$^{100}$. Experimentally, with the help of probe molecules, researches can confirm that Ti sites are imaged bright. Even though beyond the scope of this thesis, it is worth mentioning that the “reversal” tunneling site is in principle possible by modifying the tip condition and/or adjusting the tip-sample distance. The 1×2 reconstruction is normally imaged as wide strands on the surface. Under better tunneling condition, the strand can be resolved as a double-strand with a bright spot at the end. On heavily reduced surface, cross-linked structure as a bright structure can be found between 1×2 strands. Additionally, residual water in the UHV system can also induce additional bright spots which can be assigned as the hydroxyl group on the Ti row and/or dissociated proton bound to bridge oxygen.

As mentioned above, the traditional cleaning procedure (sputtering and annealing) can cause reduction of the sample and more oxygen vacancies can be created. In general, oxygen vacancies play a role of electron dopants. On the surface, the oxygen vacancies are critical as the site of chemical reaction, especially for catalysis. The surface oxygen vacancy is usually generated by removing the 2 fold coordinated bridging oxygen atom and making two 6 fold coordinated Ti atoms below become 5 fold coordinated with two unbound and unpaired electrons at the site. Thus, this site appears more reactive. The coverage of oxygen vacancies are related to the sample history, e.g. annealing temperature and total annealing time. A
maximum value are claimed to be less than 20%. In the STM image, oxygen vacancies appear as bright spots along the dark bridge oxygen row, supported by theoretical simulation\textsuperscript{101}.

The electronic structure can also be probed by PES. On a clean sample, O1s appears as a single symmetric peak; upon adsorption of residual water in UHV, a small shoulder may appear at the higher binding energy side. For Ti2p, the Coster–Kronig decay causes a much wider of Ti2p\textsubscript{3/2} than Ti2p\textsubscript{1/2}. Usually, Ti2p\textsubscript{3/2} consists of two components: one main peak assigned to Ti\textsuperscript{4+} ions at the 6 fold coordinated site and one shoulder at lower binding energy side contributed by Ti\textsuperscript{3+} ions which is ascribed to defects. In the valence band region, the oxygen 2p related orbital contribute to the region from 5 to 10 eV; the Ti3d related orbital is dominant in the region between 3 and 5 eV. The most interesting peak appears in the band gap region about 0.9 eV below the Fermi level, which stems from the defect states. The assignment of this state is still controversial. Generally, at least two types of contributions are claimed to be cause: Ti interstitials in the bulk and surface oxygen vacancies.

The recipe to prepare clean rutile (110) may vary from group to group. But in general, several steps are commonly used: 1) pre-thermal treatment in UHV to improve the conductivity, 2) sputtering and 3) annealing in UHV and/or in oxygen atmosphere. Annealing in oxygen atmosphere can heal the surface oxygen vacancies and restore the surface stoichiometry. However, special cares should be paid for the surface restoration, which is a dynamically limited process dependent on the pressure, annealing temperature and time.

### 3.2.2. Anatase (100)

Anatase also has a tetragonal unit cell with parameters a=3.782 Å and c= 9.502 Å\textsuperscript{95}. Similar to the building block of rutile, each Ti atom is six coordinated to oxygen atoms; while each oxygen atom is three coordinated to Ti atoms, which forms the octahedral building block of the crystals. The (100) surface is believed to have relatively low surface energy based on theoretical calculation. However, it does not appear in natural crystal of anatase, which two

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{anatase.png}
\caption{The anatase crystal structure (right) and STM image of (100) surface 64.5 × 64.5 nm\textsuperscript{2} (left). The insert is LEED pattern}
\end{figure}
flat top pyramid connected through the large bottom\textsuperscript{1}. The flat top is (001) surface and the eight side surfaces are (101) surface. The former is reported to have high reactivity while the latter is the most stable. Compared the other two surfaces, much less work has been carried out on the (100) surface.

The surface structure is shown in Figure 3.10. It is estimated thermodynamically less stable and significant relaxation for the upper layer is required to preserve a stable surface\textsuperscript{102}. In STM, the surface displays many bright strands over surface oriented along [010]. A 1\times n reconstruction was reported for this surface\textsuperscript{103} and was explained by a (101)-microfacet model\textsuperscript{95}. Based on our group’s work, the amount of oxygen vacancies is estimated to be low after a special sputtering process where the beam energy is increased from 400~500 eV up to 1000 eV and annealing in UHV at 550\textdegree C. Ti2p\textsubscript{3/2} shows a very small Ti\textsuperscript{3+} component\textsuperscript{103} and no obvious defect state is observed in the band gap region.
Chapter 4

Results and Discussions

In this chapter, I will briefly summarize the results of my work. Subsections 4.1 – 4.2 focus on the adsorption of phthalocyanine on bare TiO$_2$; Subsections 4.3 – 4.4 are on the modification of TiO$_2$ surface by pyridine derivatives and phthalocyanine on this modified surface; Sections 4.5 – 4.6 switch to the adsorption of the pure organic dye TPAC on bare TiO$_2$ substrate and interaction of TPAC with iodine, which simulates the solar cell interface of TiO$_2$/dye/electrolyte.

4.1. Charge Transfer of Phthalocyanine on Bare TiO$_2$

Phthalocyanines were deposited on the substrate kept at room temperature by OMBD in UHV. The thick film resembles isolated molecule due to the relative weak molecular interaction (Figure 4.1). The C1s from phthalocyanines typically show a three-peak structure, which can be deconvoluted into four components: benzene carbon (C$_B$) dominates the first peak; pyrrole carbon (C$_P$) and the shake-up of C$_B$ contribute to the second peak; the shake-up of C$_P$ is assigned to the third peak. In principle, the ratio of C$_P$ and C$_B$ should be 1:3, on the basis of chemical stoichiometry. Nevertheless, the surface sensitivity and molecular geometry can induce deviations from this value. The N1s appears as a single almost symmetric peak with a shake-up at higher binding energy. Both C1s and N1s shake-up structures correspond to the HOMO-LUMO gap, thus slightly varying as between different phthalocyanines.

![Figure 4.1 The representative of phthalocyanine C1s (a) and N1s (b) core levels collected from thick TiOPc film on rutile TiO$_2$ substrate.](image)

Previously, Palmgren et al. reported that H$_2$Pc$^{104}$ and FePc$^{105}$ experience a strong interaction on the bare rutile (110) surface. A large core level shift and vanishing of the HOMO structure were observed for these two molecules. To further investigate the phenomena, we select three
other metal-phthalocyanines along the third period: MgPc (non-transition metal, planar), TiOPc (transition metal-oxo, nonplanar) and ZnPc (fully filled d orbital transition metal, planar). In general, a similar core level shift and eliminated HOMO are found for all three molecules\(^{104-107}\). Figure 4.2 summarizes spectra for all these molecules at monolayer thickness. Curve fitting has been done to extract the interfacial and bulk components. The core level shift between interfacial and bulk component is accompanied with the disappearance of the typical shake-up structure of interfacial state, which coincidences with the quenched HOMO feature. Thus, this shift is interpreted as a charge transfer from the HOMO to the substrate.

![Figure 4.2](image)

**Figure 4.2 C1s (a) and N1s (b) of MgPc, ZnPc and TiOPc in the monolayer region; shadowed areas are the deconvoluted components: interface state (dark grey) and bulk state (light grey)**

Detailed analyses on the C\(_p\)1s, C\(_b\)1s and N1s shifts reveal that for FePc, all three peaks shift the same extent; while for ZnPc, C\(_p\) shifts only half as C\(_b\) and N. According to the molecular structure, C\(_p\) are located at the periphery and C\(_b\) and N are in the central region. Thus, ZnPc shows a site dependent core level shift. However, NEXAFS show that N K-edge shift and C\(_p\) K-edge shift are similar for ZnPc. Considering that the NEXAFS mainly reveals the initial state shift while PES is a combination of both initial and final shifts, this site dependent core level shift should be mainly ascribed to final state effects, more specifically charge transfer screening.

The 1×1 and 1×2 reconstructions are expected to influence the molecular adsorption: FePc were reported hard to image on the 1×1 surface\(^{105}\); TiOPc were found to preferentially adsorb on 1×2 strands; and CuPc could be clearly resolved on 1×2 reconstructed surface\(^{108}\). PES spectra are presented in Figure 4.3. On both 1×1 and 1×2 substrates, the core level conveys the interfacial component. But the contribution of interfacial molecules is clearly smaller on 1×2 than 1×1. This might be related to the different molecular adsorption sites, adsorption geometric and electronic structure of the substrate.
4.2. Annealing Effects on Phthalocyanine on TiO₂

Heat treatment is a critical process to fabricate organic devices. By keeping the Si/SiO₂ substrate at a temperature higher than 90°C, the performance of TiOPc based organic field effect transistor was greatly improved⁴⁴. Transitions between the polymorphic structures of TiOPc can be achieved on proper substrate, e.g. mica and sapphire, by post heat treatment⁵³,¹⁰⁹. We investigated the annealing effects on the TiOPc on TiO₂ surface at both monolayer coverage and nanometer thick films.

4.2.1. Monolayer Region

In the monolayer region, annealing at 225°C largely quenched the interfacial components, accompanied with a bulk component shift toward lower binding energy. The bonding state between TiOPc and p-type anatase TiO₂ were investigated theoretically¹¹⁰,¹¹¹. A strong bonding was suggested as the TiO moiety facing downwards to the substrate and bonded through the oxygen atom, while weak adsorption was suggested with the TiO facing upwards. Thus, it seems that the strong bond is conducted through TiO. However, our research on the planar structure phthalocyanines, e.g. FePc, MgPc and ZnPc, suggest that this interfacial state can be created without a special central moiety. Especially, our substrate is n-type TiO₂, which is also different from the simulation conditions. Then this elimination of the interfacial component amount should be due to other effects, for example, island growth and/or a phase transformation occurs, which changes the molecular geometry¹⁰⁹. On SiO₂, the TiOPc α – phase was found standing up with the benzene edge on the surface⁴⁴.

Figure 4.3 C1s spectra of TiOPc on rutile TiO₂(110) 1×1 and 1×2 reconstructed surface at different coverages. The photon energies are the same of 347 eV in the two cases.
Figure 4.4 C1s (left) and N1s (right) of TiOPc on rutile TiO$_2$(110) 1×1 (up) and 1×2 (down) reconstructed surface, before (black dots) and after (red dots) annealing.

4.2.2. Thick TiOPc Film

A 2.5 nm thick film was prepared on TiO$_2$ surface. The thickness is sufficient to block the signal of the interfacial molecules. The film as deposited appears as an amorphous structure with a large core level width. After heat treatment, all the core levels sharpen, indicating crystallization. The substrate core level and VB intensities become stronger after annealing at 250°C. It can be explained by a preferential island growth mode.$^{112}$

Accompanied by the morphological change, the electronic structure is also modified. Upon adsorption, all the molecular orbital shift toward the vacuum level, it indicates that a more p-type semiconductor is formed. As pointed out earlier, α–phase is more p-type than the other phase. Thus, it advocates the crystalline formation with a possible dominant α–phase.

Charge transfer properties were characterized by RPES. The spectra are shown in Figure 4.5 (b) and (c). The RPES data are compared with VB spectra measured at 110 eV along the binding energy scale. Three orbital regions of RPES have been divided according to the VB. The HOMO structure is located at ~ 1.7 eV binding energy, which is hardly seen in RPES due to the low cross-section at the corresponding photon energy. Meanwhile, no resonant enhancement has been observed along HOMO, which is supported by the DFT calculation that nitrogen related orbitals contribute to HOMO. In both RPES, the N1s features which are generated by the 2nd order light from the monochromator are captured. As the photon energy increase, this feature develops on the low binding energy side. Resonant enhancements are observed from the N K-edge threshold, ~ 398.3 eV. Along the first resonance around 398.5 eV, two features are observed. One is found to coincide with the orbital I in region R1, which is assigned to participator decay. The larger feature across both R2 and R3 is ascribed to spectator decay, since the whole excited state is trapped in the band gap of the TiO$_2$ and no
charge transfer is energetically favorable. The excitations into higher empty orbitals are more interesting in this case. Before annealing, the transitions to higher unoccupied orbitals appear as clear enhancements in three different regions, especially the strongest resonance in R2, as marked by the dashed line B’ and B’’. which should be the participator decay associated with the three coordinated nitrogen atoms (N₃c) in the inner ring of phthalocyanine according to the partial density of states calculated by DFT. After annealing, the spectral background is changed due to the exposed substrate signal (horizontal dashed-dotted lines). However, it will not influence the resonance signal from the resonant excitation on the molecules. The resonant enhancement associated with the transition to LUMO resembles the features before annealing. An abrupt change is found at the transition B’, where the strong enhancement is largely quenched. This is also displayed by the NEXAFS spectra, indicating that unoccupied orbital is modified upon crystallization. Thus the absorption coefficient is consequently changed regarding the modification of transition matrix from N1s core level to these N₃c related orbital.

![Figure 4.5 Resonant photoelectron spectra at N K-edge of TiOPc on TiO₂ aligned with VB spectra measured at 110 eV before (a,b) and after (c,d) annealing. Resonant transitions have been marked by vertical lines at the corresponding photon energy measured by NEXAFS. Along the binding energy scale, the VB has been divided in three regions R1 (orbital I), R2 (orbital II) and R3 (deeper orbitals, III). The horizontal dot-dashed lines through (c) and (d) indicate the substrate contribution after annealing.](image)

Theoretically, the quantitative determination of the charge transfer time is based on whether a clearly distinguishable signal between normal Auger and autoionization decays are observed. In this case, it is tricky to distinguish the normal Auger and autoionization from the RPES image. Thus the model to compare participator decay variation in different systems is preferred here. The pure participator decay intensity is obtained by integrating the intensity in the R1 region and is calibrated to the varied transition matrix by normalizing the first transition enhancement of both RPES and NEXAFS to the peak height. By assuming that the as-deposited (amorphous) film is an isolated system in which the electron does not transfer and only core hole recombination (τCH) occurs, the charge transfer time (τCT) in the annealed film can be calculated by comparing the \(I_{\text{RPES}}/I_{\text{XAS}}\) at transition B (both B’ and B’’) before and after annealing by means of Equation (4.1).
4.3. Modification of TiO$_2$ by Pyridinyl

4.3.1. 4-tert-butyl pyridine (4TBP)

As mentioned in section 3.1, the function of 4TBP is carefully characterized by different physical and chemical methods. However, the information of precise bonding site on the defected surface and the cause of the shift of the energy band of TiO$_2$ are still under investigation. Especially considering the critical role of oxygen vacancies for the TiO$_2$ catalysis application, a detailed study between 4TBP and the oxygen vacancies is required. Thereby, 4TBP was deposited on a carefully prepared rutile TiO$_2$(110) in UHV. In general case, the dominant defects on rutile (110) is bridge oxygen vacancy.

A preferential adsorption of 4TBP over the oxygen vacancies was discovered by a low dose deposition. Ti2p$_{3/2}$ (Figure 4.7 (a)) shows that the Ti$^{3+}$ component is readily quenched around 0.02 ML. Meanwhile both Ti2p and O1s (Figure 4.7 (a) and (b)), the substrate core levels, shift toward lower binding energy. This shift ceases after 0.2 ML up to the saturated surface with the extent around 0.2 eV, which matches the value reported for improvement of the solar cell performance by adding 4TBP in the electrolyte. Also, in general, the coverage of oxygen

\[ \tau_{CT} = \left( \frac{I_{RPES}/I_{XAS}}{I_{RPES}/I_{XAS}} \right)_{\text{annealed}} \cdot \tau_{CH} \]  

Where, the core hole recombination ($\tau_{CH}$) for N1s is 6 fs$^{113}$, $I_{RPES}/I_{XAS}$ values of amorphous and annealed film are 0.55 and 0.42, respectively. As a result, the charge transfer time ($\tau_{CT}$) is determined with an upper limit of 16 fs, which matches the best performance of the TiOPc OFET$^{44}$. 

Figure 4.6 Comparison of the normalized intensity of integrated RPES R1 and NEXAFS: before annealing (top) and after annealing (bottom). The dashed lines mark the background.
vacancies is no more than 20%. The following adsorption is then through the weaker coordination bond between the nitrogen and 5 fold coordinated Ti atoms (Ti$_{5f}$). This preferential adsorption is also supported by DFT simulation: the adsorption energy at the oxygen vacancies is higher than that at Ti$_{5f}$ by 120 kJ/mol. 4TBP adopts an optimized upright geometry at oxygen vacancies as those at Ti$_{5f}$.

**Figure 4.7** Ti2p$_{3/2}$ (a), O1s (b), N1s (c) and C1s (d) of 4TBP adsorbing on rutile TiO$_2$(110) surface at different coverages. (e) shows the cross-section picture of the electron distribution of 4TBP at a bridge oxygen vacancy at the corresponding adsorption geometry (f). (g) and (h) illustrate the surface band bending induced by transferring electron from the defects state to 4TBP. Dashed line is Fermi level.

From the molecular point of view, the N1s peak does not shift as the coverage increases, while C1s shifts toward higher binding energy by almost 1.0 eV. It was thus suggested that the chemical environments around the nitrogen atom in molecules adsorbed at Ti$_{5f}$ and oxygen vacancies are similar. The low binding energy found for C1s at the low coverage means that the charges at the oxygen vacancies are transferred to the upper part of the molecule, resulting in an electron rich surrounding compared to those adsorbed over Ti$_{5f}$. Nevertheless, the C1s chemical shift is too large to exclude other possibilities, for example, the molecular dipole repulsion is related to the coverage and distance and can redistribute the charge density within the molecular layer.

A comparative study was also carried on anatase (100) surface. The preferential adsorption over the oxygen vacancies is reinforced by the PES data$^{114,115}$. Less oxygen vacancies were observed on anatase(100) than rutile(110), shown by the minor Ti$_{3+}$ components in Ti2p$_{3/2}$ and little defect states in VB, which might be contributed by defects in the sublayer. The following deposition of 4TBP on anatase did not induce observable substrate band shift and quenching of the defect states, as illustrated by substrate signals. However, a C1s shift of 4TBP was found on anatase though 0.3 eV smaller than that on rutile, which should be related to the charge transfer from anatase to molecule and similar dipole repulsion within the molecular film as on rutile. The charge transfer on anatase is not as strong as the case involving oxygen vacancies on rutile, thus no band shift is observed. So, the function of 4TBP
to remove the anion like Li$^+$ should be also taken into account in the solar cell application. However, in the device, a large amount of nanocrystals are anatase but with (101) and (001) surface. Thus, further investigation is still needed.

### 4.3.2. 2,2'-bipyridine and 4,4'-bipyridine

The difference of nitrogen positions in 2,2'-Bipy and 4,4'-Bipy induced very different adsorption behavior on rutile TiO$_2$. 4,4'-Bipy dominantly adsorbs at the 1×1 perfect surface without covering the 1×2 stands (dark strands) under saturation (Figure 4.8 (a)). Its adsorption geometry was determined to be up-standing on the surface by comparing the line profile variation of PES spectra at normal and grazing emission. The molecules thus bond to the surface through one N→Ti bond with the other nitrogen pointing outwards. Each molecule approximately occupies one surface unit cell (Figure 4.8 (b) insert).

![Figure 4.8](image)

**Figure 4.8** (a) 100×100 nm$^2$ overview of 4,4'-Bipy covers the 1×1 surface of rutile TiO$_2$(110) surface, black strands are 1×2 reconstruction; (b) enlarge area with the insert showing that each 4,4'-Bipy take one surface unit cell.

On the contrary, Figure 4.9 (a) shows that 2,2'-Bipy preferentially adsorbs on the 1×2 strands developed from the 1×1 terrace edge and some under-coordinated positions at the step edges at low coverages. The preferential adsorption can still be observed at even higher coverage (Figure 4.9 (b)). By covering 2,2'-Bipy on a surface with little defects, a saturated film can be obtained. The following annealing at around 200°C desorbs those molecules with small desorption energy, leaving those which are strongly bonded to the surface. From the STM images, the molecules left by thermal desorption decorates the terraces edge, which again
supports the preferential adsorption over these sites. From the NEXAFS spectra, the 2,2’-Bipy is determined to be lying on the surface, which is also indirectly supported by the fact that 2,2’-Bipy’s PES intensity is about half of that of 4,4’-Bipy at normal emission.

Figure 4.9 (a) 2,2'-Bipy adsorbed on an aged rutile TiO$_2$(110) 1×1 surface with 1×2 strands. 2,2'-Bipy preferentially adsorbed along the 1×2 strands and 1×1 step edges. (b) at higher coverage, on aged surface. (c) saturated 2,2'-Bipy film on fresh rutile TiO$_2$(110) without 1×2 strands (d) thermal desorption of the saturated film, the left 2,2'-Bipy tends to decorate the step edges.

### 4.4 Phthalocyanine on Modified TiO$_2$(110)

As previously discussed, phthalocyanine experiences a strong charge transfer from the molecule to the substrate at the interface, showing two distinctive states in C1s and N1s. When deposited on different pyridine layers, TiOPc only shows one state as illustrated by deconvolution in both C1s and N1s. The HOMO structure of the TiOPc also appears around the monolayer region, which was completely quenched on the bare substrate. Thus, the pyridine layers effectively protect TiOPc from the oxidation.

More interestingly, the energy levels of TiOPc are found to systematically shift from each other over different pyridine layers, by 0.3 eV. As known that 4TBP and 4,4'-Bipy adopt a upright geometry while 2,2'-Bipy is lying over the surface, TiOPc on 2,2'-Bipy is expected to be more close to the surface. However, the binding energy of TiOPc/2,2'-Bipy is higher than the other two cases. It can rule out a possible influence of the final image screening effect on the photoemission peak, in which case the closer to the surface, the more efficiently molecules are screened, leading to lower binding energy. So, the systematic energy shift is determined by the energy level alignment at the interface. In other words, three types of pyridine modified the surface potential by establishing different surface dipoles. Furthermore,
it is also worth mentioning that the molecular interaction may also play an important role. For the contact parts between pyridine and phthalocyanine, the tert-butyl group is rather inert, flat lying 2,2'-Bipy is mainly π orbital and the lone pair of the nitrogen of 4,4'-Bipy can donate the electrons. Correspondingly, the interaction might have the characteristic of Van der Waals interaction and/or coordination bond.

Figure 4.10 TiOPc monolayer adsorption on 4TBP, 2,2'-Bipy and 4,4'-Bipy: C1s (a), N1s (b) and HOMO (c). Deconvoluted contribution from pyridinyls and phthalocyanine are marked as Py and Pc, respectively. (d) shows the relative peak position of TiOPc on three pyridinyls compared to the thick TiOPc film

Consistent with TiOPc on pyridines, FePc absorbed on 4,4'-Bipy is also well protected from the strong interaction, shown by the core level and preserved HOMO features in VB. One phthalocyanine usually appears as four bright lobes under STM measurement. In this case, STM shows that the FePc grows in double rows on top of 4,4'-Bipy along [001] (Figure 4.11). These double rows can grow into longer 1-D structure. Further detailed analyses indicate that some FePc molecules are tilted and overlap with each other. To the contrary, when FePc adsorbs on the bare substrate, the molecules tend to form some agglomerated structure. Additionally, the FePc on 4,4'-Bipy is less mobile than that on the bare substrate.
4.5 Interaction of Triphenylamine Dye with TiO₂

Switching from the metal phthalocyanine to a metal free organic dye, a detailed characterization of triphenylamine-based dye on rutile has been carried out. The TPAC molecules were deposited on rutile(110) kept at RT by OMBD. The molecule is anchored to the Ti⁵f through the deprotonized carboxylic group, similar to amino acids and other simple carboxylic acids. As shown in the O1s spectra (Figure 4.12), the carboxyl group appears in one single component located on the higher binding energy side of the substrate peak at 530.5 eV, which indicates that the chemical environment of the two oxygen are similar after deprotonation. Above the monolayer, the third peak develops at even higher binding energy, which should be assigned to the intact –OH in the upper layer. The development of the O1s also indicates that TPAC tends to saturate the surface, forming a condensed layer on top of TiO₂ and growing thicker. The substrate oxygen vacancies do not involve in the anchoring process in that the spectral fingerprint of defect states in the VB (Figure 4.13 (c)) is not quenched preferentially but monotonically decreases as the increased coverage, which is contrary to the case of 4TBP.
4.5.1. Coverage dependent molecular electronic structure

The electronic structure of TPAC was studied by PES. In Figure 4.13, the development of core levels and VB as increasing coverages is showed. At the low coverage, e.g. 0.2 ML, the N1s of triphenylamine nitrogen and cyano nitrogen appear at 400.0 eV and 399.0 eV, respectively. In principle, the stoichiometry suggests that the intensity ratio of the two components should be equal. However, the intensity of the cyano N1s is only half of the triphenylamine N1s, which is a good indication of a standing geometry adopted by the molecules. C1s spectra show a dominant peak at 284.8 eV with additional structure at higher binding energy. According to the electronegativity of the atom connected to the carbon, the C1s feature can be deconvoluted into three components: the dominant peak is from C-C and CH at 284.8 eV, the second is assigned to those connected to nitrogen at 285.7 eV and the third is the one connected to oxygen in the carboxylic group at 286.5 eV. The HOMO structure is located within the TiO$_2$ band gap and about 1.0 eV below the defect states (Figure 4.13 (c)).

Upon increasing the coverage, both core levels and HOMO start to shift toward higher binding energy. The peak positions are summarized in Figure 4.13 (d). As suggested by the O1s spectra, TPAC tends to cover the surface first. Thus the energy shift below 1.0 ML should be assigned to molecular interaction within the TPAC layer as the molecules become more densely packed at higher coverage. The induced upstanding geometry as discussed in the following subsection may cause less efficient screening on different ligands from the substrate. In general, the farther away from the substrate, the poorer the screening is which leads to a higher binding energy. For example, the two nitrogen components shift differently: smaller shift for cyano nitrogen; larger shift for triphenylamine nitrogen. A reasonable
4.5.2. Coverage dependent molecular configuration

NEXAFS at the N K-edge clearly illustrate a molecular geometry development. TPAC contains two nitrogen atoms, one in the triphenylamine (donor) and the other in the cyano group (acceptor). The NEXAFS spectra show changes in the molecular geometry with varying coverage, indicating a molecular configuration that evolves with coverage. The data suggest that the cyano nitrogen connected to the anchor group is much closer to the surface than the triphenylamine one in the upstanding geometry at higher coverage.
cyanoacrylic group (acceptor). In the triphenylamine part, the nitrogen bonds to three carbon in a sp² fashion hybridization, thus a π characteristic orbital is perpendicular the NC₃ plane. In the cyanoacrylic group, the cyano group orbital is conjugated with the double bond C=C, resulting in two orthogonal π orbitals, one in plane π∥ and the other out-of-plane π⊥. By using two orthogonally polarized photon beams, a coverage dependent molecular geometry was investigated. Below 0.5 ML, the cyanoacrylic group shows equally high intensity under both p and s polarization, which indicated that either this part is tilted on the surface by 54.7° or it adopts a random orientation. For the triphenylamine part, the strong peak is only observed under p polarization but not s polarization, pointing to a lying geometry of this donor part with NC₃ plane almost parallel to the surface. Above 0.5 ML, the in-plane and out-of-plane π orbitals display polarization dependence: the in-plane orbital is more populated under s polarization while the out-of plane orbital is enhanced under p polarization. It illustrates that some ordering exists on the surface and the cyanoacrylic group is tilted at 61.4°. A more severe geometry change is shown for the TPAC that the transition peak becomes invisible under p polarization and strong under s polarization, which is contrary to below 0.5 ML. The overall results support that the molecules stand up when more closely compact film is formed.

Figure 4.14 NEXAFS from TPAC at different coverages. The different polarizations of the E vector are shown as solid circles (p polarization) and empty circles (s polarization), respectively. The grazing incidence angle of the photon beam is ~7° with respect to the surface plane. The E vector of p polarization is about 7° off the surface normal, while the E vector of s polarization is parallel to the surface plane.

The curve fitting of C1s spectra also supports the upstanding geometry by taking advantage of the surface sensitivity. The comparison of different carbon component intensities is shown in Table 4-1. With the intensity of COO⁻ as the reference, \( I_{COO⁻}/I_{COO⁻} \) and \( I_{C,CH}/I_{COO⁻} \) keep around 7 and 32, respectively, below 0.5 ML. From 0.5 to 0.6 ML, an abrupt increase of those ratios is observed, especially for \( I_{C,CH}/I_{COO⁻} \). Between 0.6 and 1.0 M, the ratios become fairly stable.
again. About 85% of the carbon atoms for $I_{C,CH}$ come from triphenylamine. Thus, this dominant enhancement can be interpreted as the molecules standing up at higher coverage with the triphenylamine part further away from the substrate to which the COO$^-$ bonds. The short IMFP makes the signal of COO$^-$ largely scattered, thus an larger $I_{C,CH}/I_{COO^-}$ value.

Table 4-1 The relative intensity between the deconvoluted peak of C1s at different coverage.

<table>
<thead>
<tr>
<th>Coverage</th>
<th>$I_{COO^-}/I_{COO^-}$</th>
<th>$I_{CN}/I_{COO^-}$</th>
<th>$I_{C,C,CH}/I_{COO^-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>1</td>
<td>6.7</td>
<td>30.7</td>
</tr>
<tr>
<td>0.25</td>
<td>1</td>
<td>7.2</td>
<td>34.7</td>
</tr>
<tr>
<td>0.3</td>
<td>1</td>
<td>7.4</td>
<td>33.7</td>
</tr>
<tr>
<td>0.45</td>
<td>1</td>
<td>7.0</td>
<td>32.3</td>
</tr>
<tr>
<td>0.5</td>
<td>1</td>
<td>10.1</td>
<td>49.1</td>
</tr>
<tr>
<td>0.6</td>
<td>1</td>
<td>22.7</td>
<td>128.5</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>21.6</td>
<td>120.5</td>
</tr>
</tbody>
</table>

4.5.3. Polarization dependent charge transfer within monolayer molecules

The polarization dependent charge transfer can be revealed by the implementation of “core hole clock”. Similar to the NEXAFS measurement, REPES measurement was carried out at p and s polarization. Instead of scanning over the impinging photon energy across the N K-edge, specific incident photon energies are chosen based on the NEXAFS features, as shown in the red spots (Figure 4.15 bottom). In the REPES, a photoemission background measured several eV below N K-edge has been subtracted from the following spectra, given that the interference between the electron generated by direct excited and core-hole excited channels (Fano-like resonance) is not obvious, which usually induce a severe background variation. The participator decay (blue dashed arrow) can be easily distinguished by monitoring the enhancement peak position shifting in the kinetic energy scale with the incident photon energy. Both red and green dashed line marked the enhancement with constant kinetic energy. However, the intensity variation of the green dashed line follows that of the participator decay, but the red marked features. It indicates that the green and red marked features stem from different decay channels: spectator decay (green) and normal Auger decay (red).

The charge transfer time is also estimated by comparing the integrated RPES and NEXAFS, with their intensities of the excited states at $\pi_\perp^*$ normalized to the peak height. For the donor part probed by the photon energy between 402.5 and 404.5 eV, clear polarization dependence can be observed: p polarization does not induce a transition from N1s to this orbital while the s polarization enhances this transition. By the charge transfer time under s polarization is estimated by 1.8 fs or faster. For the acceptor part (cyanoacrylic group), the transition can be realized between 398.5 and 402.0 eV. A comparable intensity between RPES and NEXAFS indicates that the charge transfer time is close to the core hole life time, 6 fs for N1s. The charge transfer time at the donor part is about 3 times faster than at the acceptor part, which matches the picture depicted by the “push-pull” concept of this donor-acceptor complex.
Figure 4.15 Top: RPES of one monolayer TPA-C on TiO₂ surface at p polarization (left) and s polarization (right). The selected photon energies to measure RPES are marked with red dots in the RPES spectra below. Blue arrow: participator decay; Green dashed line: spectator decay; Red dashed line: normal Auger decay. Bottom: Integrated RPES intensity over the binding energy region (red) compared with NEXAFS spectra (black).

4.6. Iodine Doped Triphenylamine Dye on TiO₂

A model system to mimic the electrolyte and dye interaction has been done by coadsorption of TPAC and iodine in UHV. Upon covering the substrate with 1.0 ML TPAC, the work function is reduced around 1.0 eV. Further, doping iodine on top of TPAC, the work function can be increased again. At the saturation dosing, the maximum shift is about 0.3 eV. Similar phenomenon happens to molecular orbital. By depositing iodine on top of TPAC, all the molecular orbitals shift towards the vacuum level by the same amount of 0.3 eV. From the energy level alignment point of view, TPAC is more p-type after doping, which can be interpreted as the iodine extracts the electron from TPAC. For application, upon illumination, the charge is easier to be separated from the molecule with iodine attached, since the LUMO is at even higher position. However, this might be a drawback to regenerate the dye for the
HOMO is also elevated and the potential difference between empty HOMO and redox potential is reduced, a less driving force.

Figure 4.16 In the left, the cut-off shift of the photoelectron spectra of clean substrate (black void), 1.0 ML TPAC covered substrate (black dots) and Iodine doped 1.0 ML TPAC/TiO₂ system (grey dots). The sample is biased by -10.0 eV; in the right, the frontier molecular orbitals of TPAC 1.0 ML on TiO₂ with (red dots) and without (black dots) iodine doping.
Chapter 5

Conclusions and Future Work

By using synchrotron radiation based spectroscopy techniques and STM in UHV, we carry out a systematic study on the adsorption of photosensitive molecules on TiO$_2$ surface prepared by the organic molecular beam deposition. Two types of dye molecule have been used: classic metal-phthalocyanine and novel triphenylamine-based dye, while the substrate surfaces are controlled in 1×1 and 1×2 reconstructions and are modified by three pyridinyls: 2,2′-Bipy, 4,4′-Bipy and 4TBP. The impacts of post annealing were investigated on both morphological and electronic structure. Additionally, the iodine doping was tested to mimic the solar cell liquid/dye interface. The detailed results can be summarized into the following:

- By depositing different metal phthalocyanine on the clean rutile TiO$_2$(110), a general charge transfer phenomenon was found from the molecule to the substrate for all the tested phthalocyanines. The inner ring and periphery have different charge transfer time which is due to influence of the metal center. The one with closed d shell like Zn does not provide additional charge transfer channel as Fe which is more active due to the empty d orbital. On 1×1 and 1×2 substrate, both charge transferred interfacial state and intact molecular states were observed. But the ratio of interfacial state on 1×1 is higher than that on 1×2.

- The post thermal treatment can reduce the portion of the interfacial state, increase the degree of crystallization and shift electronic structure to be more p-type. The charge transfer properties are also modified upon the heat treatment. From amorphous to crystalline, the better molecular coupling, such as the modification of the orbitals of N3c atoms in the inner ring, enables the intermolecular ultrafast charge transfer, around 16 fs, as revealed by RPES. This result is comparable to the reported fastest TiOPc OFET.

- Three pyridinyls can all cover the rutile TiO$_2$ surface forming a saturated monolayer. However, 4TBP was found preferentially adsorbed on the bridge oxygen vacancies; 2,2′-Bipy prefers to adsorbing at the step edges and 1×2 strands; to the contrary, the Ti$_{5f}$ of the perfect 1×1 reconstructed surface is the adsorption site of 4,4′-Bipy, which avoid adsorbing at the 1×2 strands. The comparative study of 4TBP on rutile and anatase shows that the charge transfer from the oxygen vacancies to the molecules causes a substrate surface band edge shift.

- The deposition of phthalocyanine on top of pyridinyl modified surfaces can protect themselves from the severe charge transfer. Additionally, the established surface dipole and the variation of the contact parts of pyridinyls with phthalocyanine, cause
different energy level alignments of phthalocyanines. On the 4,4′-Bipy formed template, FePc change growth mode from cluster to 1D.

- The prototype of the novel pure organic dye, TPAC, has been characterized by a controlled deposition on rutile TiO$_2$. The molecule bonds to the surface with a deprotonized carboxylic group and the surface oxygen vacancies are not involved in the bonding. Below 1.0 ML, the coverage dependent molecular configuration and electronic structure were clearly revealed by PES and NEXAFS. The transition coverage is found around 0.5 ML. At 1.0 ML, the charge transfer is polarization dependent with more efficient excitation of donor part under s polarization. The “core hole clock” techniques illustrate that the charge transfer time at the donor part is ~ 1.8 fs, which is 3 times faster than that at the acceptor part.

- An Iodine doped densely packed TPAC film was investigated. The iodine is found to shift both molecular orbital and photoemission cut-off by the same extent toward the vacuum level. It can be explained as the change of the surface dipole upon the iodine dozing.

In conclusion, we investigated the adsorption of several metal phthalocyanines on TiO$_2$ with detailed analyses of the formation of oxidized interfacial states, and proposed surface engineering method to quench this state; by analyzing pyridinyl, we gained deeper understanding of the mechanism of 4TBP on the power improvement of the DSSC; by characterization of TPAC, we accumulated more knowledge about the coverage dependent variation of molecular geometry and electronic structure for the triphenylamine-based dyes. The result may benefit the design of novel organic photovoltaic devices, catalysis research and novel dye synthesis.

For future work, several directions can be approached. Firstly, it will be interesting to test the transition metal phthalocyanines in the first period in the d-block in order to further verify the generality of the charge transfer and to summarize the rule of the metal d orbital in interaction between phthalocyanine and oxide substrate. Secondly, the photosensitive molecule on anatase (101) and (001) substrate should be investigated thoroughly because these two surfaces are the dominant structures in DSSC. Thirdly, thin oxide heterojunction, such as TiO$_2$/ITO and TiO$_2$/ZnO, can also be used as substrate. Fourthly, comparison of TPAC to the ones with different linker groups should be properly addressed, which will benefit the chemical designs. Fifthly, introduce ionic liquid electrolyte into the dye/TiO$_2$ system by advanced deposition techniques and characterize the system using high pressure PES.
Bibliography


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