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**Study of surface structures of the rutile
TiO₂(110)-(1 × 2) surface and its water
adsorption reaction**

Li Fengxuan

March 2026

Study of surface structures of the rutile $\text{TiO}_2(110)-(1 \times 2)$ surface and its water adsorption reaction

A dissertation submitted to
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By

Li Fengxuan

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Abstract

This thesis summarizes the research conducted by the author in the department of systems innovation, graduate school of engineering science, the university of Osaka, namely "Study of the surface structure of rutile $\text{TiO}_2(110)-(1 \times 2)$ surface and its water adsorption reaction". The entire book consists of six chapters. The following is a summary of the contents of each chapter.

Chapter1 Introduction

Chapter1 introduces the research background of this study, gradually elaborates on the research objectives and scope, and clarifies the research goals. This chapter mainly introduces the significance of water adsorption research, and gradually delves into the $\text{TiO}_2(110)-(1 \times 2)$ surface, achieving the final goal through means such as material characterization.

Chapter2 Experimental equipment and research preparation

Chapter2 introduces the experimental setup and theoretical methods employed in this study. It focuses on the experimental preparation procedures, surface characterization techniques, and first-principles calculations. Scanning tunneling microscopy (STM) is the primary tool used for atomic-scale surface imaging, complemented by low-energy electron diffraction. The operating principles of STM and LEED are outlined, followed by a description of the specific experimental system and sample preparation. In addition, density functional theory (DFT)-based first-principles calculations and STM image simulations using the Tersoff-Hamann method.

Chapter3 Modeling and simulation of the single link on $\text{TiO}_2(110)-(1 \times 2)$ surface

Chapter3 introduces the atomic structure of the link region on the $\text{TiO}_2(110)-(1 \times 2)$ reconstructed surface by a combination of scanning tunneling microscopy (STM) and density functional theory (DFT) calculations. Based on the asymmetric reconstruction motif and comparing simulated STM images, using the Tersoff-Hamann simulation, a revised atomic model for the link region was identified. This model successfully reproduces key experimental features.

Chapter4 Modeling and simulation of the double link on $\text{TiO}_2(110)-(1 \times 2)$ surface

Chapter4 investigates the structural characteristics of double-link configurations on the $\text{TiO}_2(110)-(1 \times 2)$ surface by combining scanning tunneling microscopy (STM) and density functional theory (DFT), and further reveals the structural relationship between double-link and single-link configurations.

Chapter5 Water adsorption on $\text{TiO}_2(110)-(1 \times 2)$ surface

Chapter5 investigates water adsorption on the $\text{TiO}_2(110)-(1 \times 2)$ reconstructed surface using scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED). Water adsorption experiments were conducted at room temperature, and the temperature-dependent evolution of the link structures under water adsorption was further revealed. A previously unreported double-cross-link structure was identified, and its reversible nature was demonstrated.

Chapter6 Conclusion and prospect

Chapter6 presents the conclusion of this study and offers an outlook based on the research results.

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Chapter 1

Introduction

1.1 The significance of water adsorption

Photocatalytic technology has garnered significant attention due to its extensive application potential in solar energy conversion and environmental management. It is particularly valuable in reactions such as photocatalytic water splitting for hydrogen production, pollutant degradation, and carbon dioxide reduction. In the aforementioned photocatalytic processes, water not only serves as a reactant or reaction medium but also plays a crucial role through its adsorption, dissociation, and recombination behaviors on the surface of photocatalytic materials[1, 2]. These behaviors directly influence interfacial reaction kinetics and overall reaction efficiency[3]. Consequently, understanding the adsorption behavior of water molecules on the surfaces of photocatalytic materials is considered one of the key prerequisites for elucidating and regulating the mechanisms underlying photocatalytic reactions[4].

The adsorption process of water on solid surfaces involves molecular-surface interactions, the formation of hydrogen bond networks, and potential dissociative adsorption behaviors. These factors collectively determine the electronic structure at the interface, the chemical properties of surface active sites, and the selection of reaction pathways. A comprehensive investigation into water adsorption not only aids in elucidating the initial steps and rate controlling factors of photocatalytic reactions but also provides a theoretical basis for designing material surface structures, regulating defects, and optimizing catalytic performance. Furthermore, water adsorption behavior holds fundamental significance across various fields such as electrocatalysis, corrosion science, sensing technologies, and atmospheric chemistry. This makes it one of the core issues in surface science and catalysis research. A deep understanding of water adsorption is essential for elucidating interfacial processes. The adsorption mode and strength of water molecules directly determine the initial reaction conditions at the interface and affect subsequent charge transfer, activation energy of the reaction, and the generation and transformation of surface species[3, 5, 6]. Moreover, the differences in structure, energy levels, and active sites on different material surfaces lead to changes in water adsorption characteristics, so systematic study of water adsorption energy provides a theoretical basis for the regulation of surface interfaces[5, 7]. Mastering these laws not only helps understand the microscopic reaction mechanism but also provides important scientific guidance for designing better catalytic materials, electrochemical devices,

and moisture-resistant stable materials[8]. Therefore, water adsorption research is of irreplaceable importance in both basic scientific exploration and application technology development.

As a typical model system in the study of interface water adsorption, TiO_2 has significant advantages in many aspects [9]. Firstly, the surface structure of TiO_2 is clear and highly controllable, and its common crystal planes have been systematically studied, providing a solid foundation for the precise characterization of interfacial water adsorption behavior [10]. Secondly, under controllable conditions, TiO_2 is prone to generating surface defects such as oxygen vacancies, enabling researchers to systematically investigate the impact of these defects on the adsorption, dissociation, and interface reaction processes of water molecules. To understand the formation mechanism of surface active sites and reaction essence [11, 12]. Furthermore, the interaction between TiO_2 and water is typical. Under different experimental conditions, water molecules can undergo both molecular adsorption and dissociation adsorption. It provides an important model [9] for studying the general law of water adsorption on oxide surfaces.

Although extensive research has been conducted on the water adsorption behavior on the ideal TiO_2 crystal plane, under actual experimental conditions, the TiO_2 surface often undergoes structural reconstruction. Such reconstructed structures have a significant impact on the stability and reaction mode of water adsorption. However, relevant research is still relatively limited.

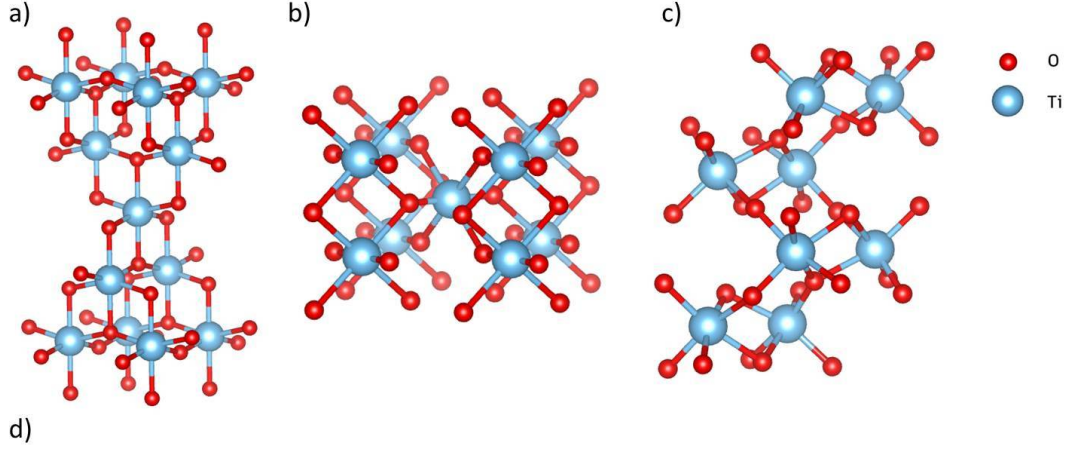
1.2 $\text{TiO}_2(110)-(1 \times 2)$ surface

Titanium dioxide (TiO_2), a representative wide-bandgap semiconductor, plays a pivotal role in fields such as photocatalysis, energy conversion, and environmental remediation. Its surface presents a variety of crystal facets whose atomic arrangements, surface defects, particularly oxygen vacancies, and adsorption behaviors strongly influence its catalytic activity. By employing strategies such as surface modification, elemental doping, and the construction of heterojunctions, the surface electronic structure and adsorption characteristics of TiO_2 can be finely tuned. These adjustments significantly enhance its performance in photocatalytic water splitting, CO_2 reduction, and the degradation of organic pollutants.

With the advancement of nanotechnology, TiO_2 has been extensively studied at the nanoscale due to its superior photocatalytic performance[13, 14]. The enhanced activity mainly stems from its significantly increased specific surface area, quantum confinement effects, and abundant surface active sites[15]. These features contribute to stronger light absorption, more efficient adsorption of reactants, and faster surface reaction kinetics.

1.2.1 Rutile TiO_2

TiO_2 exists in three main crystal structures under common conditions, namely rutile, anatase and brookite. All three structures consist of TiO_2 octahedral units, but there are significant differences in the way the octahedra are connected, crystal symmetry, thermal stability, and electronic structure. Rutile is the most thermodynamically stable crystal type and belongs to the tetragonal crystal system with



Type	Anatase	Rutile	Brookite
Crystal Structure	Tetragonal	Tetragonal	Orthorhombic
Band Gap(eV)	3.2	3.0	3.1-3.2
Absorption Edge(nm)	~388	~413	~400
Phase Transition Temp.	~600°C-700°C→Rutile	Stable	~500°C→Rutile

Figure 1.1: Ball-stick modeling of a) anatase TiO_2 , b) rutile TiO_2 , c) brookite TiO_2 . d) is the comparison of the different types of TiO_2 , including the crystal structure, band gap, absorption edge and phase transition temperature.

TiO_6 octahedra arranged in edge-sharing along the [001] direction to form a chain-like structure, which is the dominant phase at high temperatures due to its high density and smallest unit volume. Tetragonal titanite is also a tetragonal crystal system, but its octahedra are connected by corner-sharing, with a looser structure, belonging to the substable phase, which is often synthesized at low temperatures, and has a high photocatalytic activity and specific surface area. Plate titanite belongs to the rhombohedral crystal system, its structure is the most complex, thermodynamic stability is the worst, relatively rare in natural minerals, often as a small amount of intermediate phase exists.

As a thermodynamically stable phase of TiO_2 , rutile titanium dioxide has a series of unique advantages that make it valuable for applications in photocatalysis, electrode materials, surface science and other fields. Firstly, the rutile structure remains stable at high temperatures, while the other two types will transform into rutile type at high temperatures[16], and the crystal integrity can be maintained during high temperature calcination or heat treatment, which makes it suitable for devices and reaction systems that require high thermal stability[16, 17, 18]. Secondly, its dense crystal structure confers a low specific surface area and electron-hole complexation rate, which is conducive to improving the reaction selectivity in certain photothermal and electrocatalytic processes[19]. The oxygen vacancies on the rutile surface are also easily generated during vacuum annealing and can be repeatedly controlled[20]. The defect energy levels are clear, which is conducive to studying the influence of defects on water adsorption, surface reactions and electronic behavior[21]. In contrast, the defect behavior of anatase type is more complex, while the study of defects in brookite type is relatively scarce[17, 22]. Meanwhile, the rutile type surface structure is simple and easy to study,

and flat, reproducible single-crystal surfaces can be readily prepared. As a result, the rutile TiO_2 has been widely studied, which enables its optical and electronic properties to be clearly defined, making it easy for theoretical simulation[23, 24, 25].

1.2.2 $\text{TiO}_2(110)$ surface

Surface	Surface Ti coordination	Surface O coordination	Surface energy(unrelaxed) [meV/Å ²]	Surface energy(relaxed) [meV/Å ²]
(110)	5,6	2,3	30.7	15.6
(100)	5	2	33.8	19.6
(011)	5	2,3	36.9	24.4
(001)	4	2	51.4	28.9

Table 1.1: Comparison of surface energies and electronic states in rutile TiO_2 . It shows the information of surface Ti coordination and O coordination, and the surface energy as well.

The (110) surface of rutile TiO_2 is structurally regular and controllable, which is one of the most typical model systems in surface science research[18]. The surface is prone to the formation of stable oxygen vacancies, and these defects can significantly modulate its electronic structure and catalytic activity, which is an important platform for studying the relationship between surface defects and reactivity[26, 27]. Meanwhile, rutile TiO_2 has a strong UV absorption capacity, which is advantageous in the field of UV response, especially in the direction of solar energy conversion, photolysis of water for hydrogen production[18, 24, 28]. As shown in Table.1.1, the (110) plane of TiO_2 is the most stable crystal plane in the rutile phase and one of the most extensively studied surfaces[29]. Compared to other crystal planes, the (110) plane offers a series of significant advantages. First, from a thermodynamic stability perspective, the (110) plane possesses the lowest surface energy, making it the most readily formed in natural crystals[18]. Consequently, it is representative in both experimental and theoretical studies. Second, this surface exhibits regular atomic arrangement, with exposed Ti and O atoms alternating in bridging and groove positions to form a well-defined surface structure[28]. This facilitates characterization and simulation of surface reconstruction, adsorption, and catalytic reactions[30]. Compared to high-energy crystal planes like (100) or (001), the (110) surface exhibits lower oxygen vacancy formation energy, enabling stable oxygen defect formation. This more accurately reflects surface chemical behavior under reducing conditions. Additionally, the (110) surface structure facilitates electron localization and Ti^{3+} formation, which is crucial for studying photocatalytic activity, electron transport, and adsorption reactions[17, 18]. Overall, the $\text{TiO}_2(110)$ surface combines thermodynamic stability, structural characterization capability, and chemical activity advantages, making it the preferred surface for theoretical calculations and experimental studies.

It is particularly suitable for investigating surface reconstruction, defect dynamics, and catalytic mechanisms.

1.2.3 $\text{TiO}_2(110)-(1 \times 1)$ surface

The $\text{TiO}_2(110)-(1 \times 1)$ surface has been extensively investigated owing to its structural stability. In fields such as catalysis and sensors, this surface has become the main object of theoretical calculations and experimental research due to its regular atomic arrangement and relatively easy preparation[31]. There have been numerous studies on the atomic-level of the surface, the formation of oxygen vacancies, molecular adsorption and doping[32, 33]. For instance, studies have found that doping in Nb-doped TiO_2 films alters not only the local electronic structure but also affects the distribution and stability of oxygen vacancies[34]. By growing single crystal films, the adsorption patterns of water molecules or oxygen molecules near the oxygen vacancies have been revealed[35]. A large number of studies have demonstrated that surface oxygen vacancies play a crucial role in electron transfer and catalytic activation, which is essential for understanding the surface activity of TiO_2 [36]. The key affected by oxygen vacancies is the formation of Ti^{3+} [37]. The formation of surface oxygen vacancies leads to the reduction of local titanium ions, changing from Ti^{4+} to Ti^{3+} [17, 37, 38]. This process not only alters the electronic structure but also significantly affects the chemical activity of the surface[17, 37]. For example, Ti^{3+} sites can enhance the adsorption and activation of oxygen molecules and water molecules, enabling TiO_2 to exhibit higher efficiency in photocatalysis and gas sensing[38]. Therefore, the identification, regulation, and mechanism study of Ti^{3+} at the $\text{TiO}_2(110)-(1 \times 1)$ surface are core issues for understanding its catalytic performance and designing efficient functional materials.

1.2.4 $\text{TiO}_2(110)-(1 \times 2)$ surface

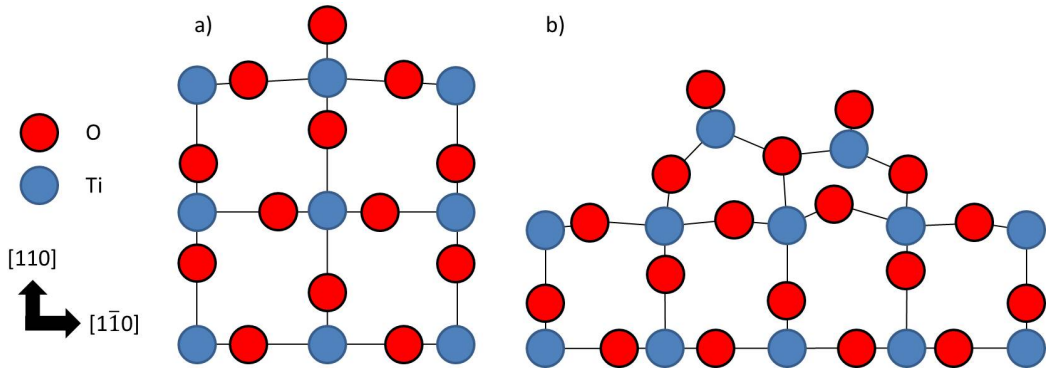


Figure 1.2: Ball-stick modeling of a) $\text{TiO}_2(110)-(1 \times 1)$ surface structure, b) $\text{TiO}_2(110)-(1 \times 2)$ surface structure.

In the reconstruction of the (110) surface, three types of reconstruction are generally recognized: (1×1) , (1×2) . In previous studies, a (1×3) reconstruction has also been observed[39]. This structure is believed to be a surface reconstruction caused by some defect, oxygen vacancy, or Ti atom arrangement, which exhibits a

3-fold periodic repetition along the $[001]$ direction. This reconstruction is unstable and is more commonly found in the process of (1×1) to (1×2) transformation. The $\text{TiO}_2(110)$ surface typically undergoes characteristic (1×2) reconstruction under high-temperature annealing or reducing conditions. This reconstruction represents a mechanism by which the crystal plane adapts to environmental changes and spontaneously reduces surface energy. The Fig.1.2 shows that compared to the original (1×1) surface, the (1×2) reconstruction exhibits an orderly rearrangement of bridging oxygen atoms along the $[001]$ direction, forming a channel like structure with a period twice that of the unit cell[40]. Concurrently, the Ti and O atoms at the top undergo minor adjustments, increasing their coordination numbers and further stabilizing the surface energy. This reconstruction typically involves oxygen vacancy formation, partially reducing surface Ti atoms to Ti^{3+} and enhancing electron localization[30, 41].

Compared to the $\text{TiO}_2(110)-(1 \times 1)$ surface, the $\text{TiO}_2(110)-(1 \times 2)$ reconstructed surface exhibits significantly different structural and electronic properties. The $\text{TiO}_2(110)-(1 \times 1)$ surface is relatively regular and stable, with orderly arrangement of Ti and O atoms on the surface and a lower distribution of oxygen vacancies[17]. Therefore, the number of Ti^{3+} ions is limited, and their electronic structure is close to that of the ideal TiO_2 crystal. However, on the $\text{TiO}_2(110)-(1 \times 2)$ surface, a typical Ti_2O_3 structure is formed[42]. This reconstruction is accompanied by an increase in oxygen vacancies, with excess electrons localized on adjacent Ti atoms, generating Ti^{3+} ions, thereby significantly altering the surface electronic state[43]. Compared to the $\text{TiO}_2(110)-(1 \times 1)$ surface, the $\text{TiO}_2(110)-(1 \times 2)$ surface has more active sites. The presence of Ti^{3+} enhances the surface's adsorption capacity for molecules such as O_2 and H_2O , and promotes electron transfer and catalytic reactions[17, 38]. Therefore, the $\text{TiO}_2(110)-(1 \times 2)$ surface exhibits significantly higher chemical activity in photocatalysis, gas adsorption, and catalytic reactions than the $\text{TiO}_2(110)-(1 \times 1)$ surface.

1.3 Researches of the $\text{TiO}_2(110)-(1 \times 2)$ surface

As shown in Fig.1.3, the scanning tunneling microscopy (STM) images reveal that the (1×2) surface mainly comprises three regions: the (1×2) region, the link region, and the defect region. The light-colored strip-like structures along the $[001]$ direction form (1×2) regions, and the distance between adjacent (1×2) columns is approximately 1.3 nm. The structure that runs horizontally along the $[\bar{1}10]$ direction and intersects perpendicularly with the (1×2) column is called the link area. There is no specific relationship on the distances between the link columns. At the same time, there will also be line defects on the surface, which will cut off the link area.

Surface properties

Due to the difficulties in preparation conditions and the unclear structure, most of the research on $\text{TiO}_2(110)-(1 \times 2)$ surface focused on theoretical calculations and comparative studies with $\text{TiO}_2(110)-(1 \times 1)$. For instance, there is a prediction regarding the (1×2) reconstruction leading to the formation of the Ti_2O_3 layer. There are predictions regarding the (1×2) reconstruction that leads to the

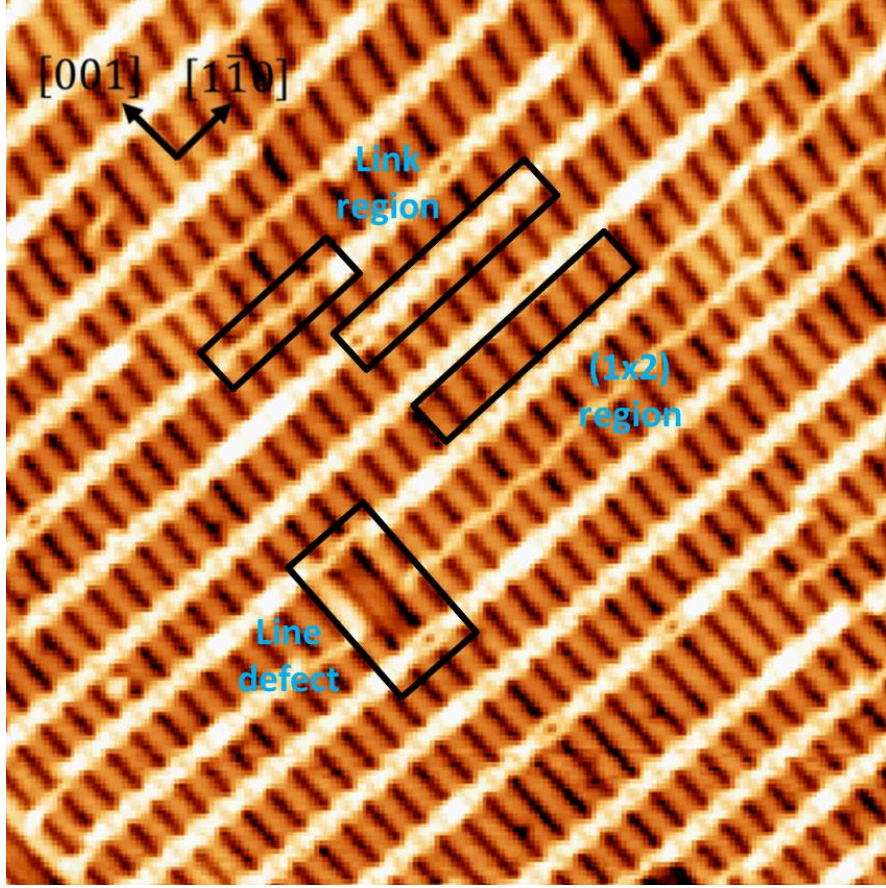


Figure 1.3: STM image of $\text{TiO}_2(110)-(1 \times 2)$ surface ($40\text{nm} \times 40\text{nm}$) with a tunneling current setpoint $I_t = 100 \text{ pA}$ and a sample bias voltage $V_s = 1.5 \text{ V}$. There are link region, (1×2) region and line defect on the surface.

formation of Ti_2O_3 layers[44], along with the calculation of the related structures. Meanwhile, in terms of the surface reactivity, Mezheny et al. investigated the reaction behavior of the $\text{TiO}_2(110)-(1 \times 2)$ surface compared with $\text{TiO}_2(110)-(1 \times 1)$ surface under ultraviolet light irradiation and found that the $\text{TiO}_2(110)-(1 \times 2)$ surface was more sensitive to the light-induced process and exhibited higher reactivity[45]. Maksymovych et al. directly observed the adsorption configuration of water molecules on the $\text{TiO}_2(110)-(1 \times 2)$ surface using a low-temperature STM, confirming that this reconstructed surface could stably adsorb water molecules and exhibited different adsorption behavior from the $\text{TiO}_2(110)-(1 \times 1)$ surface [46]. These studies have revealed the potential advantages of the $\text{TiO}_2(110)-(1 \times 2)$ surface in terms of activity and reaction properties.

Controversial structure

Initially, a (1×2) pattern emerged on the surface through high temperature annealing, which was confirmed by STM and low energy electron diffraction[41]. In the initial study, no link regions or line defects were observed. Extensive research has focused on analyzing the structure of the (1×2) region. Initially, this region was commonly considered to have a simple, symmetric structure and many researches take this model[47, 48, 49, 50, 51]. However, subsequent indepen-

dent studies through scanning probe microscopy (SPM)[42], scanning transmission electron microscope(STEM)[52], density functional theory(DFT)[44], total reflection high-energy positron diffraction(TRHEPD)[40] revealed that an asymmetric (1×2) configuration is more reasonable(Fig.1.4). The controversy over the structure has persisted for a long time, but eventually the asymmetric (1×2) structure was more widely accepted and is generally regarded as the true structure of the (1×2) region.

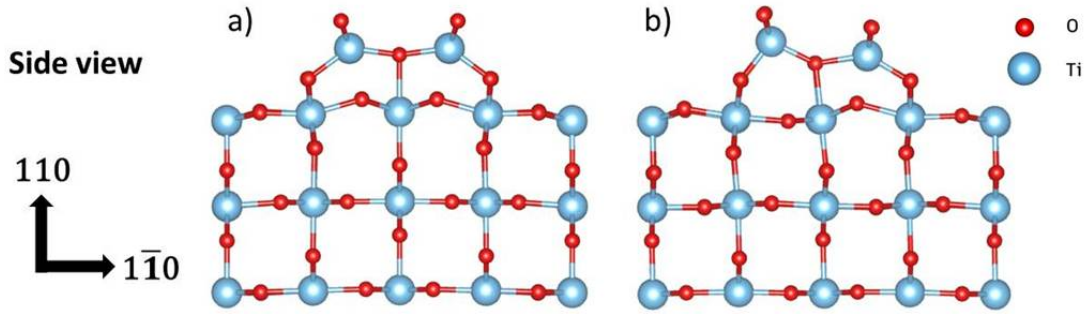


Figure 1.4: Ball-stick modeling with side view of a) symmetric $\text{TiO}_2(110)-(1 \times 2)$ structure, b) asymmetric $\text{TiO}_2(110)-(1 \times 2)$ structure proposed by previous studies. And the asymmetric $\text{TiO}_2(110)-(1 \times 2)$ structure is considered more reasonable now.

Link region

The link structure is a surface feature formed after the (1×2) reconstruction is established, through a further annealing process. Due to the limited understanding of the (1×2) structure itself, most existing studies on surface properties have focused on the overall (1×2) surface, resulting in relatively few systematic investigations of the link structure. Nevertheless, several studies have demonstrated that the link structure exhibits significant potential and research value. In experiments involving the catalytic decomposition of organic molecules, this region consistently shows higher catalytic activity compared with other surface areas, with performance exceeding that of the typical (1×2) structure[53, 54]. In the water adsorption experiments conducted under low-temperature conditions, the link structure is also considered to have an impact on this process[46]. These observations suggest that the link structure possesses distinct physicochemical properties, making it a promising target for further studies in surface chemistry and catalysis.

In terms of link region structure, differing opinions exist regarding the structure. The initial research mainly focused on the single link and X type of double link, which are more common on the $\text{TiO}_2(110)-(1 \times 2)$ surface. P. W. Murray et al. proposed the models of them[49], followed by others proposing the Ti_2O_3 -added-rows model[51, 55]. Although the Ti_2O_3 -added-rows model lacks sufficient experimental verification, it is still widely accepted.

However, theoretical research on these surfaces remains limited, and the current understanding of the link region is still highly incomplete. Although the overall structure of the (1×2) region has become relatively clear, the structure and

properties of the link region are insufficiently understood to explain its role in surface reactions. Structural investigations of the link region are further complicated by the long-standing controversy surrounding the (1×2) reconstruction and the lack of direct experimental validation. While the asymmetric (1×2) model has gained increasing acceptance[40, 42, 44, 52], most existing studies continue to rely on symmetric (1×2) structural assumptions[47, 48, 49, 50, 51], which may lead to oversimplified or inaccurate models. Moreover, the diversity and classification of link-region structures have not yet been systematically established. These unresolved issues result in significant gaps in understanding surface structural evolution and the associated reaction mechanisms. In particular, the specific ways in which the link region contributes to or enhances catalytic activity remain largely unknown, highlighting the need for further targeted experimental and theoretical investigations.

1.4 Research target and method

The adsorption of water is a key method for revealing the chemical properties of oxide surfaces, and it is of great significance for understanding the surface electronic structure, the distribution of active sites, and the reaction mechanism at the molecular level. In the study of TiO_2 , the adsorption of water molecules directly provides a theoretical basis for the photocatalytic process. Furthermore, water molecule, as the simplest and most representative adsorption molecule, its adsorption and interaction patterns are often regarded as important references for studying the surface behavior of more complex reactants. Therefore, the research on water adsorption has universal significance in surface science.

During the study of water adsorption on the interface, the relevant reactions mainly occur on the material surface and are closely related to the atomic arrangement, local structure, and defect distribution of the surface. Although macroscopic characterization methods such as LEED and XPS have provided average information about the surface, these methods are difficult to reveal the atomic-level structure of asymmetric or complex connected regions, resulting in uncertainty in the understanding of the mechanism of water molecule adsorption and reaction. Although the (1×2) region of the rutile $\text{TiO}_2(110)$ surface has been somewhat understood, the structure of the connected region is still incomplete, and this region has been proven to have catalytic potential. At the same time, there is a lack of clear interrelationships between different parts, leading to an incomplete understanding of the surface reconstruction mechanism. In this context, STM can provide direct atomic-level imaging, clearly revealing the atomic arrangement, defects, and local electronic state characteristics of the surface. First-principles calculations can optimize the possible atomic structure and analyze the electronic structure, theoretically verifying the experimental observations and quantifying the stability and active sites of the structure. By combining STM and first-principles calculations, this study can conduct a reasonable and reliable analysis of the water molecule adsorption configuration and reaction mechanism based on the clear definition of the actual surface structure of $\text{TiO}_2(110)-(1 \times 2)$, thereby overcoming the limitations of a single method and achieving a deeper understanding of the interface water adsorption process.

Based on the acquisition of a relatively reliable surface structure model, this study further combined the water adsorption experiments with in-situ imaging using STM to conduct a systematic investigation of the adsorption behavior of water molecules on the $\text{TiO}_2(110)-(1 \times 2)$ surface. By analyzing the adsorption configurations, spatial distributions of water molecules, and the induced local structural changes under different exposure conditions, the interactions between water molecules and the reconstructed surface, as well as possible surface reaction processes, were explored. Additionally, in conjunction with first-principles calculations, the observed STM characteristics and changes in the experiments were explained from a structural perspective to infer the process. Through the mutual verification of experimental characterization and theoretical calculations, this study proposed the adsorption mechanism of water molecules on the $\text{TiO}_2(110)-(1 \times 2)$ reconstructed surface at the atomic scale, providing reliable experimental evidence and theoretical support for further understanding of the related photocatalytic processes.

1.5 Composition of the thesis

Chapter 1 primarily introduces the research background and current status of the topic, elaborating on the challenges facing the relevant field. Based on this foundation, the objectives and significance of this study are clarified, and the main content and research approach are briefly outlined.

Chapter 2 focuses on the experimental methods employed in this study, introducing various experimental apparatus required for material characterization, including their working principles, functional characteristics, and applicable ranges. Emphasis is placed on the equipment actually used, along with an explanation of their roles in this research.

Chapter 3 details an investigation into surface structures by integrating STM with density functional theory DFT. In this study, STM simulation techniques were employed to examine single link structures on the $\text{TiO}_2(110)-(1 \times 2)$ reconstructed surface, focusing specifically on an asymmetric (1×2) model. A wide range of structural models, which have varying initial atomic positions and stoichiometries, were simulated to explore the energetic and structural viability of the proposed configurations. Building upon previous research, the single link model based on the asymmetric (1×2) reconstruction was successfully validated. Additionally, through comparative analysis of total energy and internal stress, the surface properties under different orientation states were evaluated, further supporting the stability and plausibility of the proposed model.

Chapter 4 presents an extended investigation into surface structures derived from single link structure. Building upon the foundational understanding of single link structure, this chapter explores the formation, composition, and characteristics of more complex double link structure. By systematically analyzing the relationships between single link structure and double link structure, including their atomic arrangements, bonding interactions, and structural transitions. The findings contribute to a more comprehensive understanding of surface, and lay the groundwork for future studies on structure-dependent surface properties.

Chapter 5 shows a detailed investigation of water molecule adsorption on the rutile

TiO₂(110)-(1 × 2) surface and the associated surface structural modifications, using STM. Upon water adsorption, bright spots appeared on the surface. However, the underlying surface structure remained largely unchanged compared to the pristine surface. Remarkably, after annealing the water-adsorbed surface at 450 °C, a previously unreported double-cross-link structure was observed. By integrating insights from existing literature, we propose a possible formation mechanism that the double-cross-link structure likely results from surface oxidation reactions triggered by hydroxyl groups during the high temperature annealing process.

Chapter 6 presents the overall conclusions of this study and provides an outlook on potential future research directions. And next comes the research outputs and acknowledgement. The Appendix includes selected parameter files used in the first-principles calculations, serving as a reference for reproducibility and further computational work.

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Chapter 2

Experimental equipment and research preparation

2.1 Chapter description

This chapter focuses on introducing the experimental setup used in this research, experimental preparation procedures, and the relevant content regarding first-principles calculations. Special emphasis is placed on the key instruments used for material surface characterization. The main tool is the scanning tunneling microscope (STM), which can image the surface atomic structure with high resolution. Complementary to STM is low-energy electron diffraction (LEED), which is used as an auxiliary technique for analyzing and confirming the surface crystal structure and detecting structural changes at the atomic scale. Section 2.2 details STM operating principles. This section begins by elaborating on the quantum tunneling effect, which is the foundation for the operation of the STM, enabling the detection of surface topography with atomic-level precision. Subsequently, it describes the specific STM system used in this experiment, including its key components, operational parameters, and the environment in which the measurements are conducted. Finally, it explains the preparation of the probe, sample, and target surface for this experiment. Section 2.3 introduces the fundamental concepts of low energy electron diffraction. This technique relies on the diffraction of low-energy electrons from the periodic surface lattice, allowing for the determination of surface symmetry, reconstruction patterns, and the presence of defects. The principles of LEED are explained to provide a theoretical foundation for interpreting the experimental diffraction patterns obtained during this study. Section 2.4 introduces the first-principles calculation method and STM simulation adopted in this study. The calculation is based on density functional theory (DFT). On this basis, STM images are simulated using the Tersoff–Hamann method to compare the theoretical results with the experimental STM images, and to analyze the surface reconstruction and defect distribution characteristics. At the same time, the software used in this research is also introduced.

2.2 Scanning Tunneling Microscopy (STM)

STM, a type of scanning probe microscopy (SPM), has had a profound impact on the scientific community since its invention in 1981 [1, 2]. Today, STM is widely used for atomic-resolution imaging of conductive and semiconductor surfaces. As a result, STM is commonly used to study surface structures and defects at the nanoscale. By utilizing a sharp tip to scan the sample point-by-point, STM can obtain at the nanoscale[2]. Since its inception, STM has been used in a variety of fields including physics[3], chemistry[4], materials science[5] and biology[6]. Especially in nanoscale research, STM provides sub-nanometer resolution imaging capabilities, enabling direct observation of atomic arrangements on material surfaces[7]. This makes STM indispensable for structural characterization of nanomaterials, electronic property studies, and atomic-scale fabrication. For instance, in cutting-edge fields such as two-dimensional materials[8], single atom catalysts[9], and molecular electronic devices[10], STM is frequently employed to reveal key nanoscale phenomena including interface density of states distribution, defect structures, and charge transfer behavior. This provides crucial support for designing and optimizing functional materials.

2.2.1 The principle of STM

Tunneling effect and tunneling current

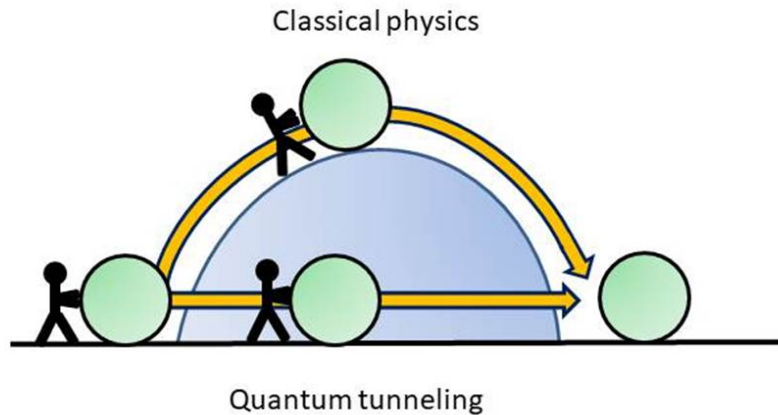


Figure 2.1: Overview of differences in energy transfer between classical physics and quantum tunneling

In classical mechanics, the motion of a particle strictly follows the law of energy conservation. When the total energy of a particle is less than the height of a potential barrier, the particle cannot surmount the barrier and will be completely reflected. This description treats the particle as a point-like object with well-defined position and momentum, excluding any possibility of it entering the classically forbidden region[11].

However, in quantum mechanics, particles exhibit wave particle duality, and their behavior is no longer governed by deterministic classical trajectories, but instead

described by a wavefunction. The wavefunction provides the probability amplitude for finding the particle at a given position in space. When a particle with energy $E < V_0$ encounters a potential barrier, its wavefunction inside the barrier does not vanish; instead, it decays exponentially.

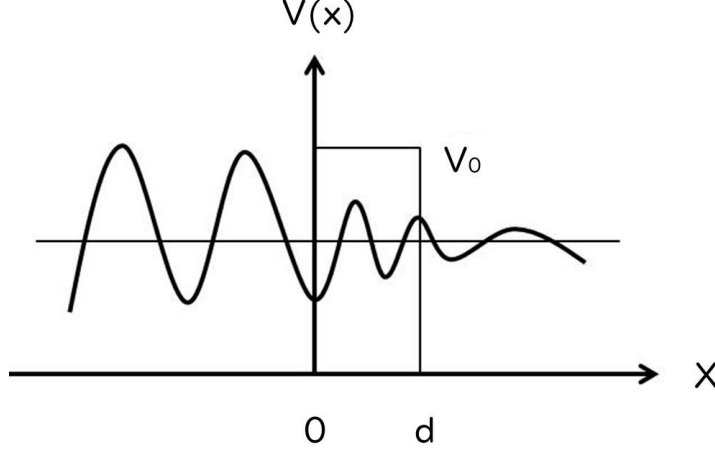


Figure 2.2: Principle of tunneling effect is shown in the figure. A one-dimensional rectangular potential barrier with width d and height V_0 , and the energy will be decreasing.

As shown in Fig.2.2, consider a one-dimensional rectangular potential barrier with width d and height V_0 . When an electron with energy E less than V_0 is incident from the left, its behavior is governed by the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad (2.1)$$

where

- $\hbar$ is the reduced Planck constant,
- m is the electron mass,
- $\psi(x)$ is the wavefunction,
- $V(x)$ is the potential energy as a function of position,
- E is the total energy of the electron.

Inside the barrier region $0 < x < d$, where $V(x) = V_0$, the Schrödinger equation reduces to

$$\frac{d^2\psi(x)}{dx^2} = \frac{2m(V_0 - E)}{\hbar^2} \psi(x) = \kappa^2 \psi(x) \quad (2.2)$$

with the decay constant.

Because the wavefunction beyond the barrier remains nonzero, there is a finite probability for the electron to tunnel through the barrier, giving rise to the tunneling current.

When two metallic or conductive surfaces are separated by a vacuum or an ultrathin insulating layer, applying a voltage V between them induces a tunneling current. In 1961, Bardeen derived the fundamental expression for the tunneling current. Based on this, Tersoff-Hamann further developed a model applicable to STM. Under the weak coupling approximation, the tunneling current I can be expressed as:

$$I \propto \int_{-\infty}^{+\infty} \rho_s(E) \rho_t(E - eV) |M|^2 [f(E) - f(E - eV)] dE \quad (2.3)$$

where

- $\rho_s(E)$ is the local density of states (LDOS) of the sample at energy E ,
- $\rho_t(E)$ is the density of states of the tip at energy E ,
- M is the matrix element representing the tunneling probability of electrons between the sample and the tip,
- $f(E)$ is the Fermi-Dirac distribution function,
- V is the applied bias voltage,
- e is the elementary charge.

At low temperatures and low bias voltages ($eV \ll k_B T$), the expression simplifies to

$$I \propto V \cdot \rho_s(E_F) \cdot \rho_t(E_F) \cdot e^{-2\kappa d} \quad (2.4)$$

where

- E_F is the Fermi energy,
- d is the distance between the tip and the sample surface,
- $\kappa = \sqrt{\frac{2m\phi}{\hbar^2}}$ is the decay constant,
- ϕ is the effective work function (in electron volts, eV),
- m is the electron mass,
- $\hbar$ is the reduced Planck constant.

Thus, the tunneling current decays exponentially with increasing tip-sample separation:

$$I \propto e^{-2\kappa d} \quad (2.5)$$

This exponential dependence enables atomic-scale resolution: a tip displacement of a few angstroms changes the current from picoamperes to nanoamperes, enabling extremely high spatial resolution in STM measurements.

The STM is a surface imaging technique based on the quantum tunneling effect. Its core components include an ultra-sharp metallic tip, a sample stage, a current

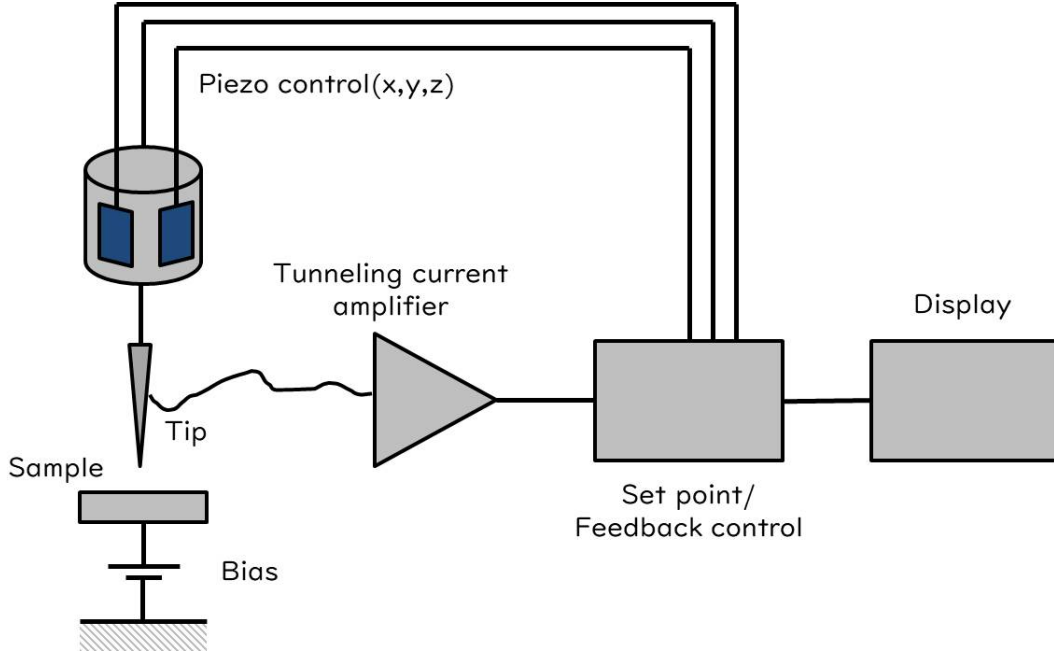


Figure 2.3: Schematic of the STM system. When the distance of the sample and the tip gets close enough, it will have a tunneling current. The tunneling current will change with the change of the distance between the tip and the sample. Through the computer display, we can know the surface structure of the sample by the change of the tunneling current.

amplifier, a feedback system, and control and imaging systems. The tip is usually made of tungsten or platinum-iridium alloy, with the apex width only one or two atoms wide, allowing atomic-scale interaction with the sample surface. The sample stage is equipped with high-precision piezoelectric actuators capable of nanometer-scale three-dimensional (xyz) scanning, precisely controlling the relative position between the tip and the sample.

Fig.2.3 shows the schematic of the STM. When the tip approaches the sample surface and a bias voltage is applied, electrons tunnel through the vacuum gap, generating an extremely weak tunneling current. Since the tunneling current depends very sensitively on the distance between the tip and the sample, which is exponentially decaying with distance, STM uses this current as a feedback signal to continuously adjust the tip height in real time, maintaining a constant current and thus mapping the surface morphology of the sample. The current amplifier amplifies this usually microampere level weak current for measurement and analysis.

As shown in Fig.2.4, STM mainly operates in two modes: the constant current mode and the constant height mode. In the constant current mode, the feedback system continuously adjusts the tip height $z(x,y)$ to keep the tunneling current constant. The variation in tip height is then used to map the surface morphology. This mode provides stable imaging and adapts well to surface topography variations but has relatively slower scanning speeds and requires a responsive and precise feedback system[12].

In contrast, the constant height mode keeps the tip height fixed and directly records the tunneling current $I(x,y)$ variations over different scan points. This

mode offers faster scanning speeds and is suitable for relatively flat surfaces; however, it is prone to distortions or tip collisions when scanning rougher surfaces. Especially when scanning soft, organic molecules or semiconductor surfaces, this may introduce artifacts or damage the sample structure.

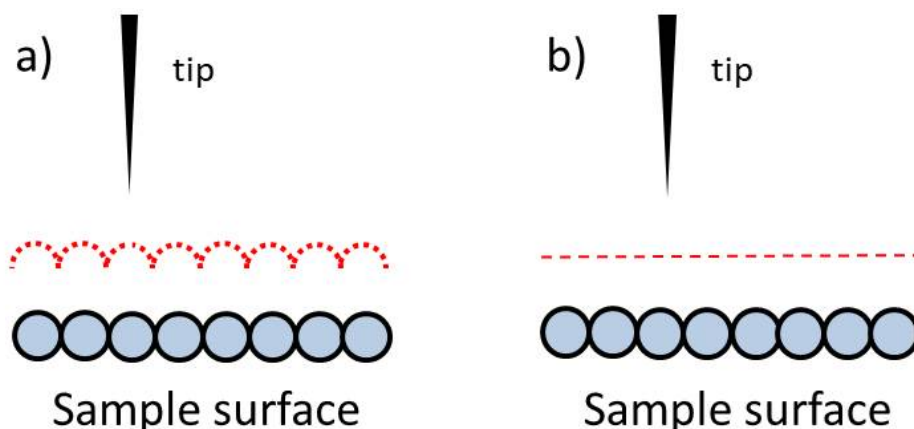


Figure 2.4: Schematic of the two work mode of STM. a) is the constant current mode and b) is the constant height mode.

Constant current mode maintains stability and high precision throughout the imaging process. This mode effectively adapts to various surface irregularities and complex structures, ensuring a stable distance between the tip and the sample during imaging. This prevents signal fluctuations and minimizes the risk of tip collisions. Not only does this yield more authentic and reliable images, but it also enhances spatial resolution, enabling clear visualization of atomic-level surface details. Additionally, the superior signal stability in constant current mode helps reduce noise, thereby improving imaging quality and data reproducibility. Therefore, constant current mode was selected for STM operation in this experiment.

2.2.2 STM system for experiments

Fig.2.5 illustrates the configuration of the experimental ultra-high vacuum (UHV) STM system, comprising several interconnected chambers: the observation chamber (OBS), preparation chamber (PREP), load-lock chamber (LL), low-energy electron diffraction chamber (LEED), and pulsed laser deposition chamber (PLD). The STM apparatus is housed within the OBS chamber, which is normally isolated by a closed valve to prevent contamination when not in use. An ion pump maintains the ultra-high vacuum, typically achieving base pressure below 1×10^{-11} Torr.

Sample and tip preparation occur in the PREP chamber, equipped with an argon gas line for sputter cleaning and a heater for thermal treatment. The valve between the PREP and LEED chambers remains closed during preparation to preserve vacuum integrity, while the valve linking PREP and LL chambers stays open. An ion pump ensures sustained vacuum throughout the process.

The LL chamber facilitates sample and tip transfer, connected to an external mechanical pump for initial evacuation before entering the high-vacuum system. For

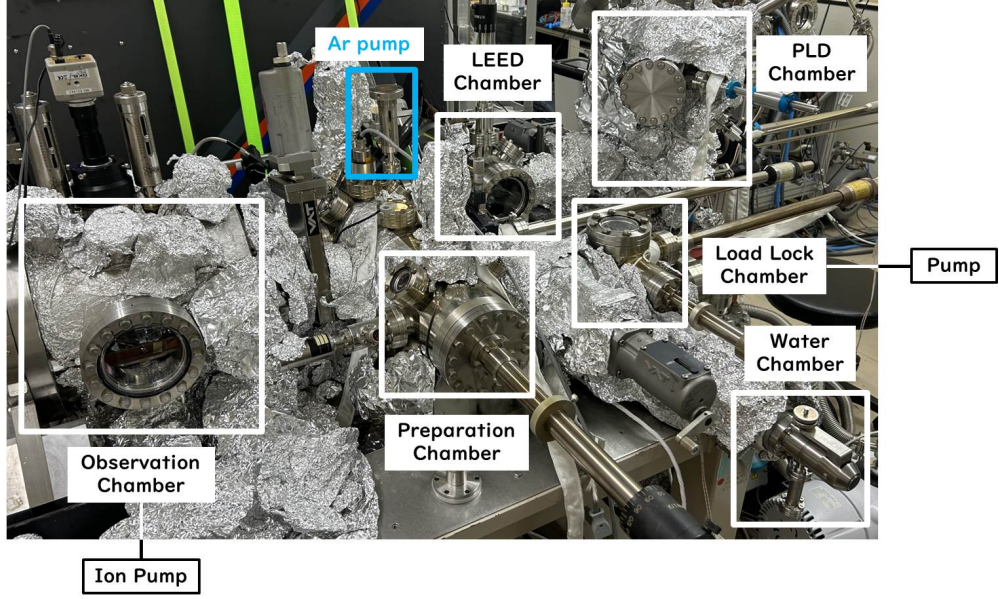


Figure 2.5: STM system from left to right is observation chamber, preparation chamber, load lock chamber. Additionally, there is LEED chamber connected to preparation chamber, and PLD chamber on the right. Water chamber is connected to load lock chamber. The argon chamber is connected to the preparation chamber. Observation chamber and preparation chamber have independent ion pumps to maintain vacuum, and the load lock chamber is connected to a pump to maintain overall vacuum. There are valves between the chambers which can be closed individually.

experiments involving water exposure, a dedicated water chamber, which contains water purified via the freeze-pump-thaw method, is connected to the LL chamber but kept isolated by a closed valve except during use.

The LEED chamber, used for surface crystallography, connects directly to the PREP chamber through a normally closed valve and to the PLD chamber on the opposite side, which is designated for thin film growth. Although the PLD equipment is not utilized in this experiment, the chamber serves as a temporary sample storage space.

This modular, isolated chamber design ensures vacuum integrity while enabling flexible sample preparation, modification, and in-situ characterization under strictly controlled conditions.

2.2.3 Research preparation

Freeze-pump-thaw method

Before the experiments, the water chamber was degassed using the freeze-pump-thaw (FPT) method to remove dissolved impurity gases that could interfere with water adsorption measurements and subsequent analyses. The FPT technique, a widely recognized and reliable degassing method, operates based on Henry's law, which describes the temperature and pressure dependence of gas solubility in liquids [13]. In this procedure, water was frozen in liquid N_2 , evacuated under vacuum to remove liberated gases, and then thawed to release remaining dissolved

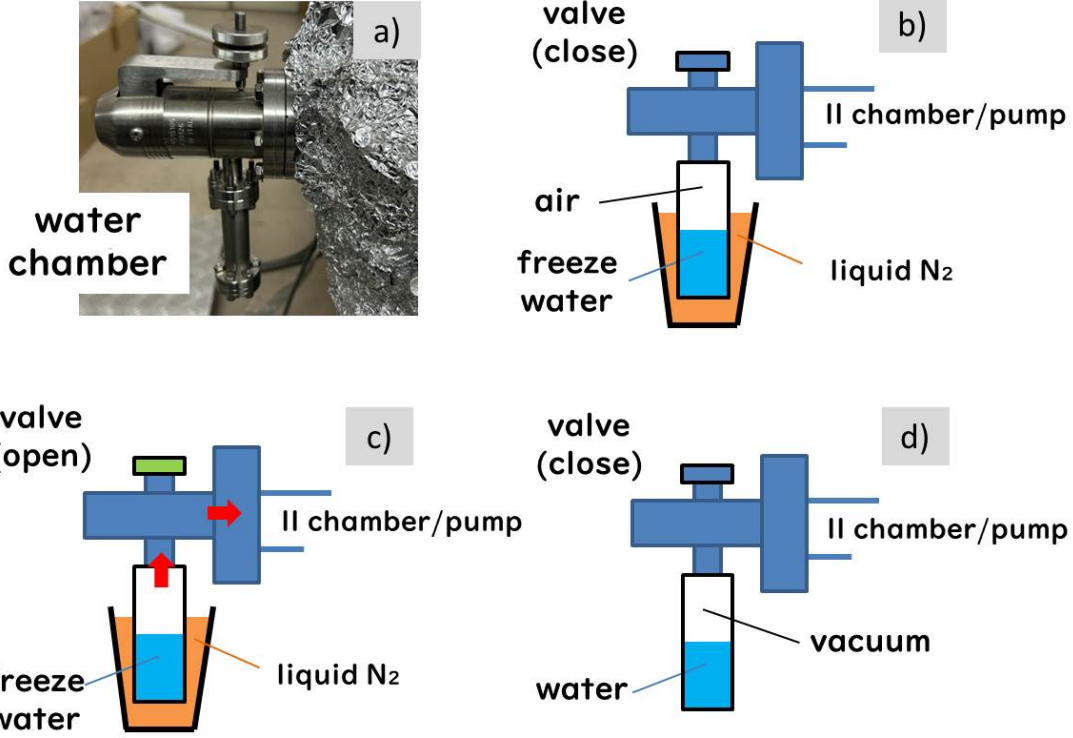


Figure 2.6: Schematic diagram of the freeze-pump-thaw method. a) refers to the water chamber in our experimental equipment. Panels b), c), and d) show the process that the freeze-thaw-pump method operates in this experiment.

species (Fig.2.6). This FPT cycle was repeated three to five times to ensure the effective removal of residual gases, providing high-purity water essential for reliable surface adsorption studies and minimizing the influence of trace gases on experimental results.

STM probe

In STM, the performance of the probe directly determines the imaging resolution, stability and experimental reproducibility. Two common probe materials are tungsten (W) and platinum-iridium alloy (PtIr), which have been reported to exhibit significant differences in physical properties, chemical stability, preparation methods, and applicable environments[14, 15, 16]. Tungsten probes are widely used in the STM field due to their high hardness and excellent electrical conductivity, especially for UHV environments. The main advantages of tungsten probes are their low cost, simple preparation, and especially the rapid acquisition of sharp probe tips by electrochemical etching[14]. However, tungsten is highly susceptible to oxidation in air, and the formation of a surface oxide layer can seriously affect its electron transfer performance and image quality, which is requiring high-temperature annealing or ion bombardment before use. When studying the surface of TiO₂, tungsten probes are commonly used for high-resolution imaging of surface morphology due to their strong conductivity, easy preparation by electrochemical etching and high sharpness, and they can better inject electrons into the conduction band of n-type TiO₂, which is conducive to the study of its localized

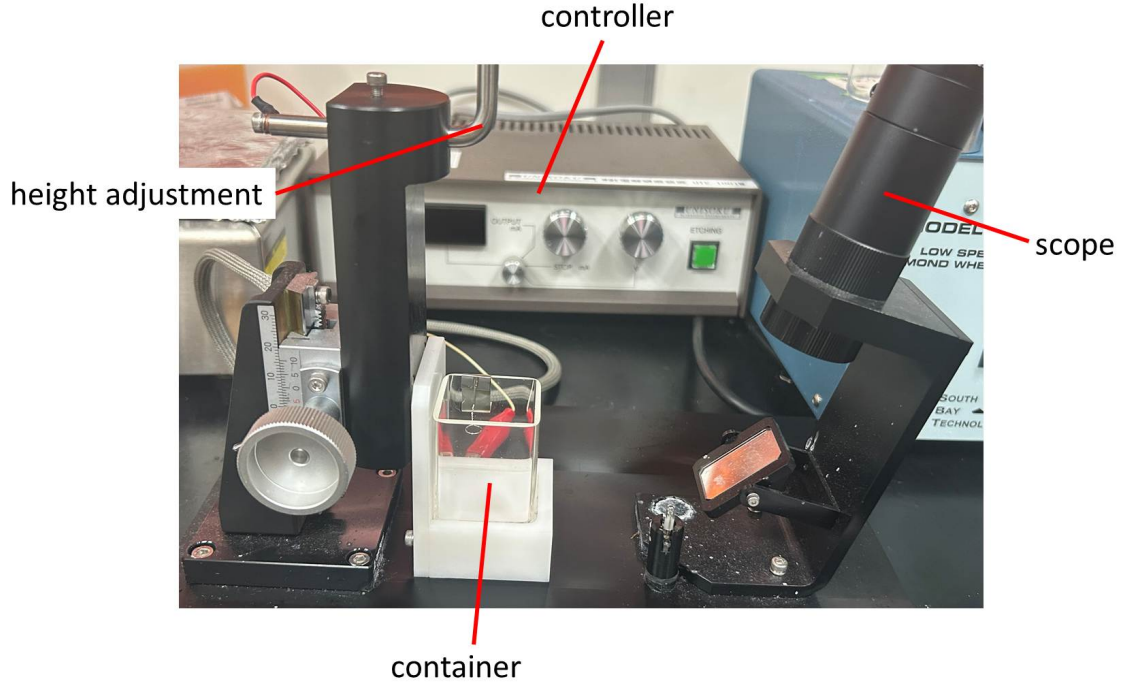


Figure 2.7: Illustration of a probe-making apparatus comprising two primary parts: a controller for regulating process parameters, and an operating table where the physical probe fabrication takes place.

electronic state[17]. Therefore, a W probe was chosen in this experiment [18, 19]. The W probe used in this study was a homemade W one by electrochemical corrosion method, and the preparation setup is shown in Fig.2.7. The probe fabrication unit consists of two main components: a controller and an operating table. The controller regulates key electrical parameters, including the cut-off current and the initial voltage. In this study, an initial voltage of 12 V and a cut-off current of 0 A were selected based on preliminary testing.

As shown in Fig.2.8, the metal plate is placed outside the container and connected to the power supply. Inside the container, a hard metal wire is used to connect it to a metal ring. Place the metal ring approximately 1 mm away from the inner side wall. Ensure that the liquid surface is in contact with the metal ring and the liquid level is slightly lower than the metal ring. We will take a tungsten wire approximately 10 cm in length. First, we will use sandpaper to polish its surface to remove the oxide layer and impurities on the surface. Then, we will place it in ultra-pure water and clean it using the ultrasonic cleaning method. The tungsten wire is fixed using the height adjustment, and its position is made to be at the center of the metal ring. The liquid inside the container is 1.2 N KOH solution. The wire height was adjusted so that approximately 2 mm of its length was immersed in the solution before initiating the electrochemical etching process. After etching, the tungsten wire will melt at the liquid surface. Then, it was examined under a microscope to confirm its shape and sharpness. Then, the qualified probes will be fixed and assembled, and the excess parts will be trimmed off. The completed probe was mounted into the vacuum system. Prior to STM measurements, surface cleaning was performed by sputtering with Ar^+ ions at a

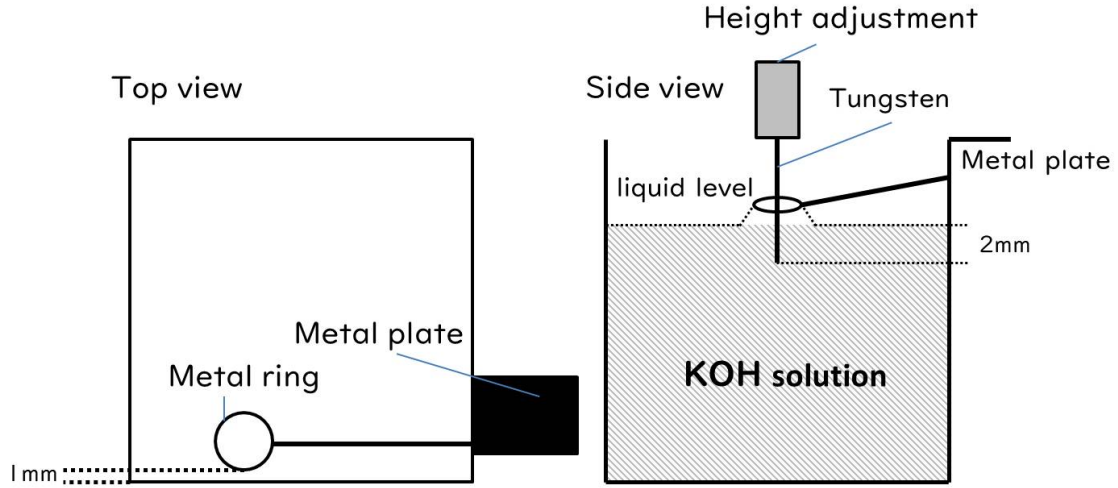


Figure 2.8: Schematic diagram of the etching experimental operation. The left side is the perspective view from top, and the right side is the perspective view from the side.



Figure 2.9: Physical image of the probe mounted on the holder.

partial pressure of 1×10^{-7} Torr for five minutes. Fig.2.9 shows the final assembled probe.

TiO₂ sample

Since many metal oxides are electrical insulators, they cannot be directly heated using conventional direct current (DC) heating, which typically relies on current passing through a conductive sample to generate Joule heat. To address this limitation, an indirect heating method was employed in this study. Specifically, a metallic heating film was wrapped around the sample, allowing heat to be transferred via thermal conduction from the film, which carries the heating current, to the non-conductive sample.

The samples used in this experiment are metal oxides that require precise high-temperature treatment during annealing and surface preparation. To meet these thermal demands, tungsten (W) was initially selected as the heating film material

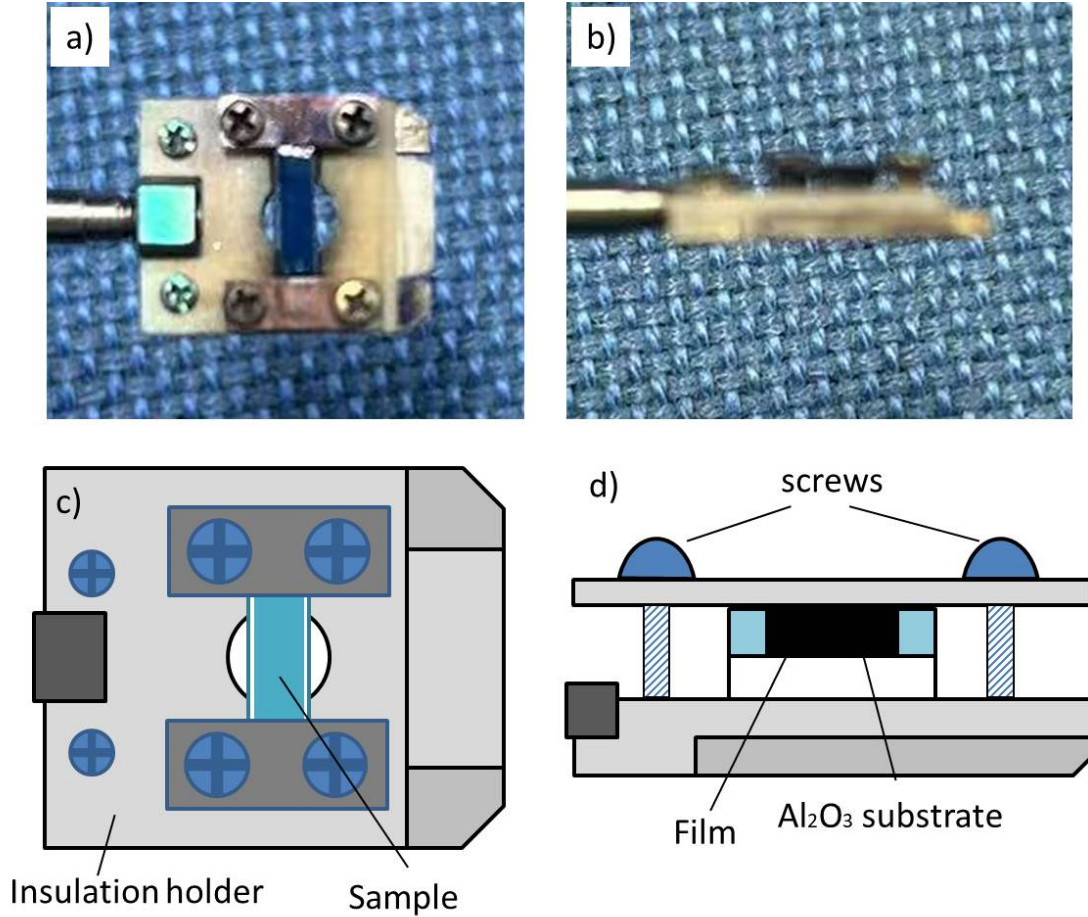


Figure 2.10: a) and c) show the actual top view image and the schematic, respectively, and b) and d) present the actual side view image and the schematic, respectively.

due to its high melting point (3422 °C), excellent thermal stability, and chemical inertness under vacuum and reducing environments. However, to accelerate heating and cooling rates, molybdenum (Mo) was later introduced as an alternative. Mo offers a slightly lower melting point (2623 °C) but has a higher thermal conductivity, which facilitates faster heat transfer and more responsive temperature control. Experimental tests confirmed that Mo met the thermal requirements of the process while significantly reducing heat-up and cool-down durations.

A schematic diagram of the sample assembly is shown in Fig.2.10. The base platform is composed of an electrically insulating material, and a layer of alumina (Al₂O₃) is placed between the base and the sample to provide both mechanical support and thermal insulation during high-temperature heating. The metallic heating film is sandwiched between the alumina substrate and the sample and is slightly wrapped around the edges of the sample to enhance uniform heat distribution. The entire assembly is firmly fixed in the center of a custom-designed sample holder and secured to the bottom electrode using screws. This design ensures good mechanical stability, reliable electrical connection, and efficient thermal conduction during operation.

Program for auto anneal

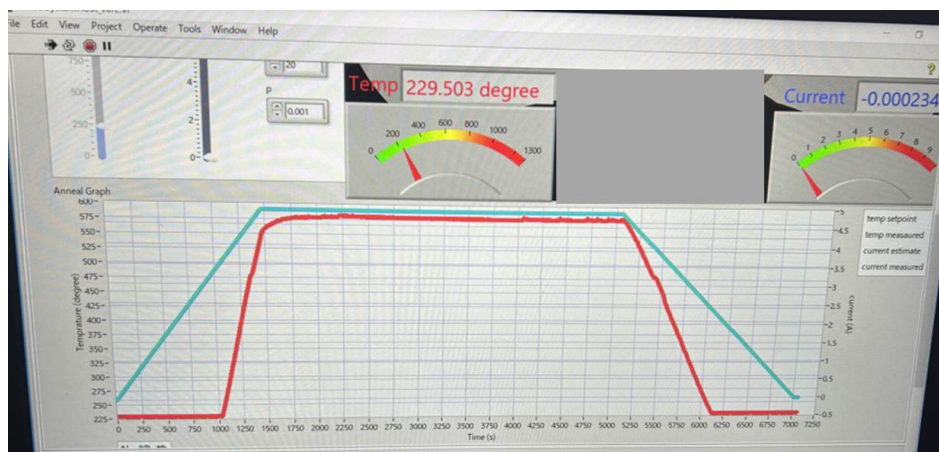


Figure 2.11: Main interface of the automatic temperature control system, the red line in the figure is the temperature change curve, the blue line is the current change curve, the chart shows the temperature and current change process of one annealing.

Given the stringent surface preparation conditions required in this study, particularly those involving extended cycles of heating, annealing, and controlled cooling a custom LabVIEW-based automation program was developed to manage the entire procedure. Manual control of such processes is not only labor-intensive but also prone to variability, especially when precise timing and thermal ramping are critical. Automation was therefore essential for achieving the level of reproducibility and process stability demanded by surface science experiments.

The main interface of the program is shown in Fig.2.11. The software enables fine-grained control over all stages of the surface preparation process. Specifically, it allows the user to define the rate of temperature increase and decrease, dwell times at specified setpoints, and current ramp profiles, all through an intuitive graphical interface. These parameters can be adjusted according to experimental requirements and saved as templates for future use.

By automatically regulating the ramping behavior of current and temperature, the program ensures smooth transitions between thermal stages, effectively avoiding thermal shocks or abrupt fluctuations that could damage the sample or negatively impact surface reconstruction quality. This results in more uniform and defect-free surfaces, which is crucial for high-resolution STM and other surface-sensitive characterization techniques.

In addition to improving thermal control and minimizing manual input, the automation significantly reduces total preparation time. Once initiated, the system can run unattended, freeing up researchers for other tasks. Furthermore, the program continuously logs key parameters, such as current, voltage, temperature, and timing, into a structured data file. This allows for full traceability of each preparation cycle and facilitates post-experiment analysis, troubleshooting, or replication under identical conditions. Such data logging also supports long-term optimization of surface preparation protocols by enabling comparative studies across multiple experiments.

Overall, the introduction of this automated system not only improves experimental efficiency and consistency but also enhances the scientific rigor of the surface preparation process by eliminating variability associated with manual operation.

TiO₂(110)-(1 × 2) surface

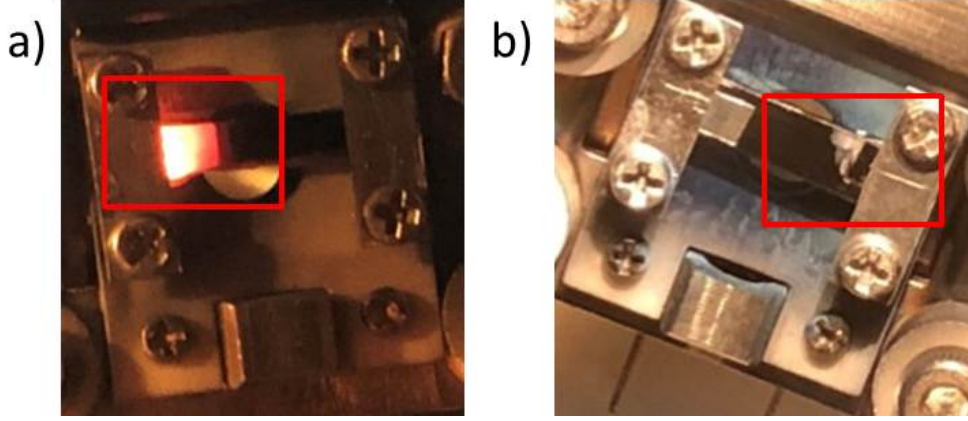


Figure 2.12: Actual cases of sample damage. a) is a fracture, resulting in uneven heating. One side was heated while the other side had a relatively low temperature. This condition prevented the process of annealing. b) is caused by heating temperature and assembly issues during preparation, leading to cracking and melting, with obvious missing areas on the surface.

The TiO₂(110)-(1 × 2) surface usually cannot be directly obtained under normal conditions. Instead, it is formed by inducing a reconfiguration from a clean TiO₂(110)-(1 × 1) surface through appropriate surface treatment. The currently known preparation methods include annealing treatment, ion beam bombardment, and pulsed laser deposition (PLD). After conducting actual experiments, we chose the most stable method in our experiment environment. We choose the ion sputtering and annealing cycle, which involves first using Ar⁺ sputtering (0.5 keV-1.5 keV depending on surface status) to remove surface contamination, and then annealing at a temperature of 800 to 1100 °C, thereby forming a periodic strip-like (1 × 2) reconstruction along the [001] direction[20, 21]. In addition to the sputtering and annealing process, high temperature annealing under controlled oxygen partial pressure can also yield a (1 × 2) surface, with the degree of reconfiguration being finely controlled by adjusting the oxygen vacancy concentration[22]. In this experiment, we used the conventional sputtering annealing method. Because this method requires high temperature treatment of the samples, it makes the sample preparation very difficult. During the high-temperature heating process, sample damage often occurs, as shown in Fig.2.12. The samples may have many damage situations, such as fractures caused by uneven heating (Fig.2.12.a) and surface defects (Fig.2.12.b), etc. This situation can sometimes even cause the screws on the holder and the bottom plate to burn out.

In this experiment, the automatic temperature control program described above was used to regulate the annealing process. This ensured that the rate of current change during the heating and cooling process remained constant and was carried out at a slow speed(0.3 A/s). Meanwhile, the status of the sample was monitored

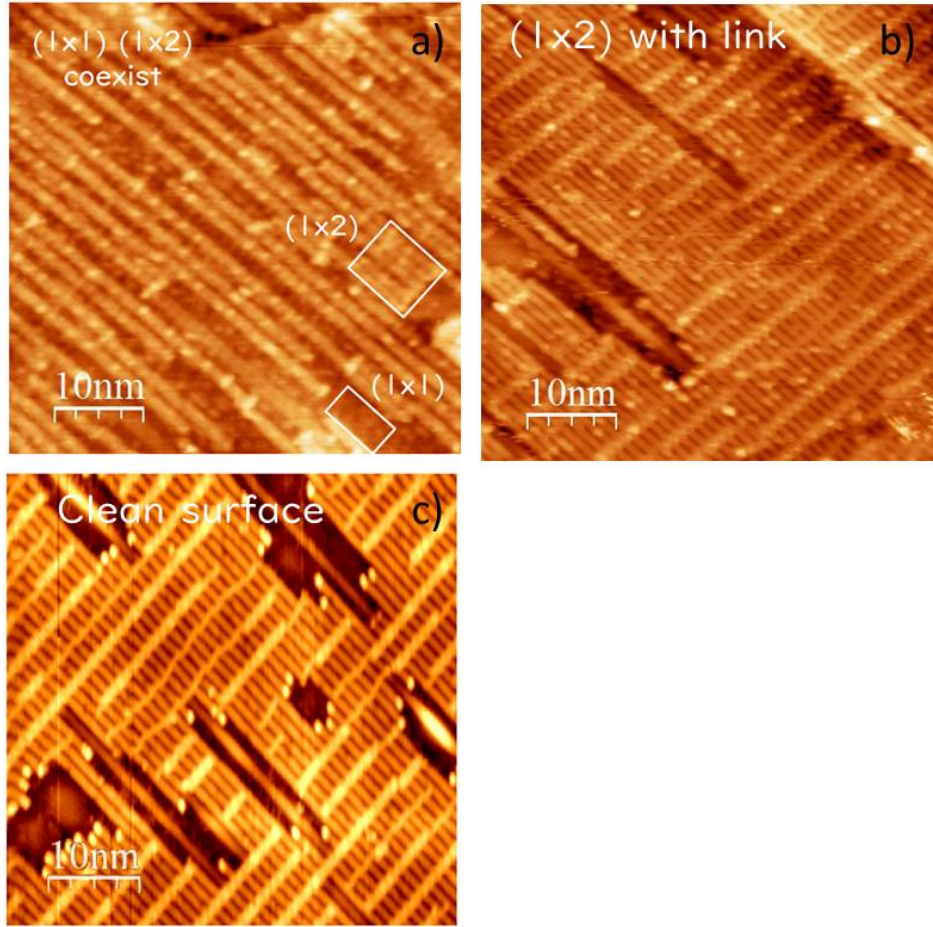


Figure 2.13: STM images of the $\text{TiO}_2(110)-(1 \times 2)$ surface formed : a) Surface where (1×1) and (1×2) coexist, with a strip-like (1×2) structure formed on the upper part of the (1×1) structure; b) (1×2) surface with links, but impurity atoms still exist; c) Clean (1×2) surface with links. The tunneling current setpoint was 100 pA. The sample bias voltage was 1.5 V.

in real time during the heating process(900 °C), and the annealing temperature was maintained at a relatively low level to increase the success rate of sample fabrication. Usually, from a clean (1×1) surface, a striped structure would appear, and then a state of coexistence of (1×1) and (1×2) would be formed, as shown in Fig.2.12. Through multiple sputtering annealing processes, large areas of (1×2) surfaces with links could be formed. During the sample preparation process, there are still some problems that cannot be solved and insufficient explanations are lacking. For example, if there are many impurity atoms during the process of making (1×2) surfaces, sometimes the sputtering annealing method cannot make them clean. These problems make it more difficult to obtain clean samples. Usually, we frequently use STM to observe the images during the process to ensure that the obtained surface is a clean surface.

2.3 Low-energy electron diffraction(LEED)

LEED is an experimental tool used to determine the surface structure of single crystals. LEED can be used to monitor structural changes on surfaces before and

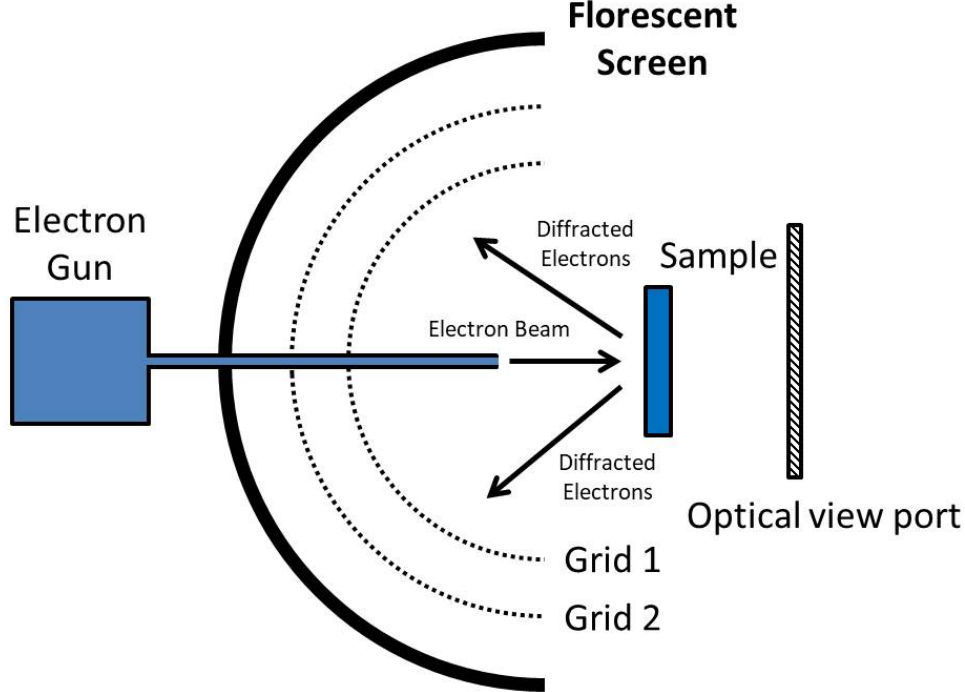


Figure 2.14: Schematic diagram of low-energy electron diffraction experimental setup. Electrons emitted from the electron gun are accelerated to the same energy by an electric field, then focused into an electron beam by a set of electron lenses and directed onto the sample surface. Electrons scattered by the sample surface form a diffraction pattern.

after reactions, revealing adsorption, desorption, or restructuring processes. Its advantages include high resolution, strong surface sensitivity, and the ability to visually reflect surface order[23, 24, 25]. Low-energy electrons readily interact with atoms. If they penetrate too deeply into the material, they are absorbed by the body. However, if they scatter back from the top two or three layers, they carry valuable information about the arrangement of the atoms on the surface. Low-energy electrons are highly sensitive to surface layers and are ideal for analyzing surface atomic arrangements. According to the de Broglie hypothesis[26, 27], electrons exhibit wave-like properties. The wavelength of an electron is given by:

$$\lambda = \frac{h}{\sqrt{2m_e E}}$$

where:

- h is Planck's constant,
- m_e is the electron mass,

- E is the energy of the electron.

For low-energy electrons (typically in the range of 20–200 eV), the wavelength is comparable to the atomic spacing in a crystal (about 1 Å), making diffraction phenomena noticeable. When the low-energy electron beam is incident perpendicularly on a single crystal surface, the periodic potential formed by the surface atoms causes the electron waves to scatter. The scattered electron waves form diffraction patterns when certain diffraction conditions are met. These diffraction conditions are similar to Bragg's law in X-ray diffraction[28], but applied to the surface, with the two-dimensional Bragg condition given by:

$$\vec{k}_{\text{out}} - \vec{k}_{\text{in}} = \vec{G}_{\parallel}$$

where:

- $\vec{k}_{\text{in}}$ and $\vec{k}_{\text{out}}$ are the wave vectors of the incident and scattered electrons, respectively,
- $\vec{G}_{\parallel}$ is the two-dimensional reciprocal lattice vector parallel to the surface.

This formula indicates that the scattering condition depends on the periodic arrangement of the surface atoms, i.e., the reciprocal lattice vectors in the reciprocal space.

Under high-vacuum conditions, the electron gun emits low-energy electron beams that strike the sample surface. After elastic scattering, the electron waves form a series of diffraction spots. By analyzing the distribution, intensity, and shape of these spots, the arrangement and structure of surface atoms can be deduced (Fig.2.14). LEED patterns consist of a series of diffraction spots whose distribution is closely related to the symmetry and periodicity of the surface lattice. The intensity of the spots is influenced not only by the positions of surface atoms but also by atomic vibrations, the distribution of adsorbates, and possible surface reconstruction effects. Changes in the pattern can reflect changes in the atomic arrangement on the surface, such as surface reconstruction or the presence of defects[29, 30].

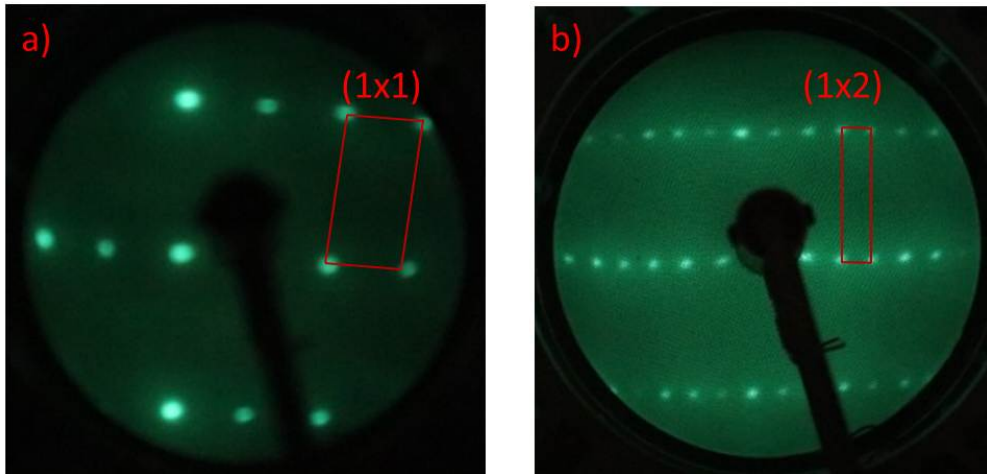


Figure 2.15: LEED pattern of a) $\text{TiO}_2(110)-(1 \times 1)$ surface, b) $\text{TiO}_2(110)-(1 \times 2)$ surface

Figure 2.15 shows the LEED patterns of the $\text{TiO}_2(110)-(1 \times 1)$ surface and the $\text{TiO}_2(110)-(1 \times 2)$ surface. The LEED image of the $\text{TiO}_2(110)-(1 \times 1)$ surface presents a regular and clear diffraction spot array. Compared with the $\text{TiO}_2(110)-(1 \times 1)$ surface, the $\text{TiO}_2(110)-(1 \times 2)$ surface has additional diffraction spots in the transverse direction in the LEED image. These spots are located between the characteristic spots of the $\text{TiO}_2(110)-(1 \times 1)$ surface, indicating that the real space periodicity of the surface in this direction has doubled. Correspondingly, the reciprocal lattice point distance in this direction in the LEED image is reduced to half of that of the $\text{TiO}_2(110)-(1 \times 1)$ surface, while the period in the vertical direction remains unchanged.

2.4 First-principles calculation

STM provides direct observation of surface morphology and local electronic states at the atomic-level, but its imaging contrast depends on the local density of states, making direct determination of atomic structure difficult. First-principles calculations can predict atomic geometries, electronic structures, and energetic stability, and STM simulation techniques allow these theoretical predictions to be connected with experimental observations. By combining STM with first-principles calculations, experimental STM images can be interpreted through theoretical simulations, linking bright and dark features to specific atomic positions, thereby reliably confirming the surface atomic structure and improving understanding of surface structure and properties.

First-principles calculations, also known as *ab initio* methods, refer to a class of computational approaches that predict and analyze the properties of materials or molecular systems based on fundamental physical laws, which are the primarily quantum mechanics and electronic structure theory without relying on any empirical parameters or experimental data. These methods start from the most essential particle interactions and typically involve solving the Schrödinger equation or its approximations to obtain the total energy, atomic structure, excited-state behavior, and other relevant physical or chemical properties of the system.

The theoretical foundation of first-principles calculations can be traced back to the development of quantum mechanics in the early 20th century, which provided a rigorous mathematical framework for describing the behavior of microscopic particles. However, due to the sheer complexity of real materials involving large numbers of interacting electrons and nuclei, that direct solutions to the many-body Schrödinger equation are mathematically and computationally infeasible.

With the development of computational mathematics—including numerical analysis, linear algebra, and integration techniques—first-principles methods have evolved into a variety of effective models operating at different levels of approximation and computational cost. These include methods such as Hartree–Fock[31, 32, 33], Møller–Plesset perturbation theory (MP2)[34], coupled-cluster theory (CCSD(T))[35, 36], and quantum Monte Carlo (QMC)[37], all of which offer varying balances between accuracy and computational demand.

It was not until 1964 that Hohenberg and Kohn proposed density functional theory (DFT), followed by the introduction of the Kohn–Sham equations by Kohn and Sham in 1965, that first-principles calculations became practically feasible[38, 39].

This theoretical framework transformed the complex many electron problem into a system of effective single particle equations and described the system in terms of electron density rather than many-body wavefunctions, greatly reducing the computational complexity.

Subsequently, with advancements in computational technology, improvements in numerical algorithms, and the development of widely used software platforms such as VASP, ABINIT and CASTEP, first-principles methods rapidly evolved into standard tools for materials research. Researchers can now predict a wide range of key material properties based on the chemical composition and crystal structure, without requiring any prior experimental input, including structural stability, band structure, density of states, formation energy, and interfacial characteristics.

In recent years, first-principles approaches have continued to progress toward higher accuracy and broader applicability across multiple length and time scales. Beyond the conventional approximations such as generalized gradient approximation(GGA)[40] and local density approximation(LDA)[41] for the exchange correlation functional, more advanced methods have been developed, including hybrid functionals[42, 43], DFT+U[44, 45], self-consistent GW[46, 47], and ab initio molecular dynamics[48]. These developments have significantly extended the applicability of first-principles calculations beyond ideal crystalline systems to include defects, surfaces, interfaces, adsorption phenomena, and non-equilibrium processes.

2.4.1 Density functional theory(DFT)

First-principles calculations are a computational method for investigating the properties of materials and molecules without relying on empirical parameters and directly from the fundamental laws of quantum mechanics. Its goal is to predict the structure and properties of atomic and electronic systems from the most fundamental laws of physics, primarily the Schrödinger equation. Density Functional Theory (DFT) is a specific and efficient theoretical framework for realizing first-principles calculations. It greatly reduces the computational difficulty by simplifying the complex problem of multi-electron systems into the study of electron density, making first-principles calculations of large-scale, complex systems possible.

DFT is one of the most influential and widely used computational methods in quantum chemistry and condensed matter physics. As a theoretical framework for studying the electronic structure of atoms, molecules and solids, DFT has become a cornerstone for exploring material properties and chemical phenomena. Its applications are wide-ranging, covering a variety of fields such as physics, chemistry, biology and materials science.

The theoretical foundations of modern DFT began in 1964 with the formulation of two landmark theorems by Pierre Hohenberg and Walter Kohn, which shifted the focus of quantum mechanics from the complex many-body wave function to the simpler electron[39].

The first Hohenberg–Kohn theorem states that, for a given external potential $V_{\text{ext}}(\mathbf{r})$, the ground-state electron density $\rho(\mathbf{r})$ uniquely determines all properties of the system in its ground state.

The second Hohenberg–Kohn theorem establishes that there exists an energy func-

tional $E[\rho]$ which reaches its minimum at the true ground-state density $\rho_0(\mathbf{r})$:

$$E[\rho] = T[\rho] + E_{\text{ext}}[\rho] + E_{\text{H}}[\rho] + E_{\text{xc}}[\rho] \quad (2.6)$$

where:

- $T[\rho]$ is the kinetic energy functional;
- $E_{\text{ext}}[\rho] = \int \rho(\mathbf{r})V_{\text{ext}}(\mathbf{r}) d\mathbf{r}$ represents the interaction energy with the external potential;
- $E_{\text{H}}[\rho]$ is the classical Coulomb (Hartree) energy;
- $E_{\text{xc}}[\rho]$ is the exchange–correlation energy functional, which accounts for complex many-body quantum interactions among electrons.

In 1965, Walter Kohn and Lu Jeu Sham proposed a practical method for calculating electron densities based on the Hornberger-Kohn framework[38]. The Kohn-Sham method makes DFT computationally feasible by introducing the assumption that non-interacting electrons move in an effective potential field, which approximates a complex multi-electron system into an easily handled system. The Kohn-Sham equation is the central equation in density functional theory. Based on the Hohenberg-Kohn theorem, the energy of the many-electron system is expressed as a generalization of the electron density. Then, a reference system without interaction is introduced, whose electron density is the same as that of the real multielectronic system. By the variational principle, the energy generalization is polarized to obtain the Kohn-Sham equation in the form:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{s}}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}) \quad (2.7)$$

The $\hbar$ is reduced planck constant, the m is the mass of the electron, the ∇ is the Laplacian operator, representing the kinetic energy operator in quantum mechanics. The $\varphi_i(\mathbf{r})$ is the Kohn–Sham orbital for the i -th electron, which means a single-particle wavefunction. The ε_i is the orbital energy associated with the i -th orbital. And the $V_{\text{s}}(\mathbf{r})$ is the effective potential (Kohn–Sham potential), which includes the external potential $V_{\text{ext}}(\mathbf{r})$, the Hartree (electrostatic) potential $V_{\text{H}}(\mathbf{r})$ [38, 32] and the exchange-correlation potential $V_{\text{xc}}(\mathbf{r})$.

$$V_{\text{s}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) \quad (2.8)$$

The Kohn-Sham equation transforms the multi-electron problem into a set of single-particle equations, allowing us to obtain properties such as ground state energy and electron density of multi-electron systems by solving these single-particle equations. It plays a key role in the practical application of density functional theory and provides an important theoretical basis for calculating the electronic structure, chemical bonding, and optical properties of materials. By choosing a suitable approximation for the exchange-correlation potential, the Kohn-Sham equation is able to accurately describe the properties of various multielectronic systems to a certain extent, and has been widely used in physics, chemistry, materials science and other fields.

2.4.2 Tersoff–Hamann theory

The Tersoff–Hamann theoretical model is a simplified but physically sound theoretical framework for describing the relationship between the tunneling current and the Local Density of States (LDOS) of a sample in 1983[49]. Based on Bardeen’s tunneling formalism[50], the theory simplifies the STM tip as a spherically symmetric s -orbital localized at the apex of the tip and assumes weak coupling between the tip and the sample. One of the central assumptions of the Tersoff–Hamann model is to reduce the STM probe end to an s -orbit state with spherical symmetry and located at a point in space. This assumption greatly simplifies the representation of the tunneling matrix element such that the tunneling current is only related to the LDOS of the sample surface at the probe location. Specifically, the model ignores the effects of probe geometry, atomic structure, and orbital symmetry on the tunneling current, thereby reducing the problem of simulating the STM image to that of spatially integrating the LDOS of the sample. Although this simplification may not be accurate in some cases, especially in high-resolution or probe functionalization experiments, the model has been shown to have good qualitative and semi-quantitative explanatory power for most routine STM simulations.

In the constant-current mode, the Tersoff–Hamann theory assumes that the tunneling current I is proportional to the local density of states (LDOS) of the sample at the STM tip position $\mathbf{r}$ near the Fermi energy ϵ_F , expressed as:

$$I \propto \int_{\epsilon_F}^{\epsilon_F + eV} \rho(\mathbf{r}, E) dE \quad (2.9)$$

Here, eV is the applied bias voltage, and $\rho(\mathbf{r}, E)$ is the LDOS at the tip position $\mathbf{r}$ and energy E . For positive bias (empty-state imaging), the integration range is from ϵ_F to $\epsilon_F + eV$, whereas for negative bias (filled-state imaging), it is from $\epsilon_F + eV$ to ϵ_F .

In the low-temperature and small-bias limit, the above expression further simplifies to:

$$I \propto \rho(\mathbf{r}, \epsilon_F) \quad (2.10)$$

Therefore, STM images essentially reflect the spatial distribution of the LDOS at the sample surface beneath the tip. In practical simulations, wavefunctions and charge densities are first calculated by VASP to integrate $\rho(\mathbf{r}, E)$ over the energy window defined by the applied bias, thereby generating theoretical STM images for comparison with experimental results.

This result implies that STM imaging essentially probes the spatial distribution of the sample’s LDOS near the Fermi level, rather than its total charge density. The Tersoff–Hamann model has become widely used in combination with first-principles calculations, particularly density functional theory (DFT), for simulating STM images. By computing the LDOS from electronic structure calculations and applying the Tersoff–Hamann approximation, theoretical STM images can be generated for direct comparison with experimental results. This enables a detailed understanding of surface reconstructions, adsorbate interactions, defect states, and other atomic-scale phenomena relevant to surface science and nanotechnology.

STM image simulation

Since the generation of STM images relies on high-precision wavefunction and charge density distributions, charge density (CHGCAR) and wavefunction (WAVECAR) files requiring processing are large in size. Therefore, when utilizing VASP to simulate STM images, calculations are typically performed in two steps to ensure computational efficiency. The first step involves performing conventional self-consistent field calculations on the optimized files to obtain electronic structure information, including CHGCAR and wavefunction WAVECAR files. The second step involves further processing based on these output files, where parameters required for STM simulation are input into the input file (INCAR). This step does not involve structural optimization or recalculating the self-consistent field. Instead, it extracts the LDOS near the Fermi level using the Tersoff–Hamann model, simulates the current distribution as the probe scans the surface, and thereby generates the STM image. The appendix at the end of this document will present the INCAR files from our two simulations to illustrate the parameters used in this simulation optimization.

2.4.3 Software

Vienna Ab initio Simulation Package(VASP)

The Vienna Ab-initio Simulation Package (VASP) is a commercial software for materials simulation developed by the Hafner group at the University of Vienna[51]. It is based on DFT[38] and employs the plane-wave pseudopotential method to perform molecular dynamics and first-principles electronic structure calculations. VASP is currently one of the most widely used commercial tools in materials modeling and computational materials science research.

Unlike Car–Parrinello Molecular Dynamics (CPMD)[48], VASP accurately solves the instantaneous electronic ground state of the system at each molecular dynamics time step. After calculating the atomic forces and the stress tensor of the system with high precision, it relaxes the atomic positions toward the instantaneous ground-state configuration.

The core idea of VASP is to solve the ground state electronic structure of the material system based on DFT, efficiently describe the interaction between electrons and ions through the plane wave basis set and pseudomorphic or projector augmented wave (PAW) method[52], and solve the Kohn-Sham equation by using k -point sampling in the Brillouin zone and self-consistent iteration (SCF)[53]. Thus, the total energy, optimal structure and electron density of the system can be obtained, providing a basis for the calculation of properties such as energy band, density of states, magnetism and charge distribution. At the same time, efficient numerical algorithms and parallel computing are combined to achieve precise simulation of large-scale systems.

In VASP, the commonly used computational method is to combine the PAW method [52] with the Generalized Gradient Approximation (GGA) functional[40]. GGA is an improved DFT exchange-correlation energy approximation method. It not only relies on the electron density itself but also takes into account the gradient information of the electron density, thereby describing the distribution of electrons in space more accurately than the local density approximation[40, 38].

GGA is usually closer to the experimental results than LDA when calculating material properties such as crystal structure, bond length, binding energy and band structure. It is a widely used commutation-correlation functional in first-principles calculations. PAW method is one of the main point of the VASP. The PAW method was proposed by P. E. Blochl in 1994 as a computational approach that combines the advantages of pseudopotential method and all-electronic method[52]. Its core objective is to significantly reduce the computational load while ensuring near-full electronic computing accuracy, making the calculation of complex systems feasible. In the calculation of electronic structure in quantum mechanics, the electron wave function near the atomic nucleus oscillates violently and changes rapidly. To precisely describe these wave functions, a large number of plane wave basis sets need to be used, which will lead to a huge amount of computation. The traditional pseudopotential method makes the valence electron wave function smooth in the core region by replacing the true potential with a smooth effective potential, thereby reducing the number of required basis sets. However, this method may lose some accuracy in certain cases, especially when it comes to chemical bonds, charge density distribution or magnetic analysis. The basic idea of the PAW method is to establish an augmentation region near each atom, use all-electron description within the region, and apply a smooth pseudowave function description outside the region[54]. This means that outside the pseudopotential, the wave function is exactly the same as the pseudopotential function. Near the atomic nucleus, the true all-electron features are restored through projection and enhancement operations. This approach not only retains the efficiency of pseudopotential calculation but also enables the accurate calculation of charge density, magnetic moment and chemical bond properties like the all-electronic method. Compared with the traditional ultra-soft pseudopotential (US-PP) method[54, 55], the PAW method has higher transferability and stability. Although USPP also introduces compensation charges to reduce the number of plane waves, it often lacks accuracy when dealing with strongly localized states. PAW performs better in describing problems such as chemical bonds, magnetism and charge distribution because it can restore the all-electron wave function. These approaches significantly reduce the number of plane waves required in calculations, especially for systems involving transition metals or first-row elements of the periodic table.

The main input files of VASP include:

- INCAR: Controls calculation parameters;
- POSCAR: Defines the atomic structure;
- POTCAR: Contains pseudopotential information for each element;
- KPOINTS: The k -point sampling method is used for Brillouin zone integration.

KPOINT is a very core input file in VASP calculation, which is used to control the sampling mode and density of the Brillouin Zone[53]. In the calculation of periodic systems based on DFT, the crystal structure is periodically repetitive in space, so the electron wave function satisfies Bloch's theorem[56]. This means that the electronic state can be marked by the wave vector k in the momentum space. The physical quantities of the system, such as energy and electron density,

all need to be integrated at these k -points within the first Brillouin zone[54]. Selecting and distributing these discrete k -points is a very important step in the VASP calculation. Since the Brillouin zone is a continuous three-dimensional space, theoretically, integration should be carried out at all k -points, but this is impossible in actual calculations. VASP approximately completes the integration by selecting a limited number of representative k points in the Brillouin zone and weighting the average based on the symmetry of the system. This discretization process is called k -point sampling. The higher the sampling density, the more accurate the integration, but the computational load also increases accordingly. Therefore, the selection of KPOINT is a key step in balancing computational efficiency and accuracy.

The output files, such as OUTCAR(a comprehensive output file, almost containing all the information about the program's operation), CONTCAR(optimized structure file), CHGCAR(the distribution of charge density in real space), and WAVECAR(the Kohn-Sham wave function information of the system), can be used for further analysis of structure, charge distribution, and STM image simulations.

Thanks to its excellent parallel performance, comprehensive functionality, and well-documented user resources, VASP has become one of the most widely used first-principles simulation platforms in materials physics, surface science, and nanoscience.

p4vasp

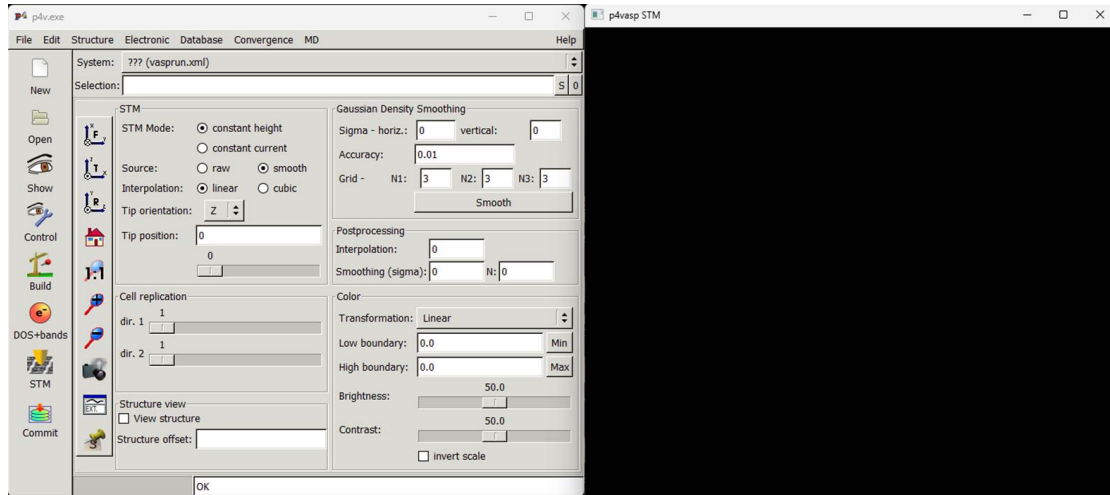


Figure 2.16: Launch screen of p4vasp in the window system, the left side of the parameter settings section, the right side of the STM simulation image section.

p4vasp is a software based on open source python program designed for processing and visualizing VASP calculation results. It supports graphical display of crystal structure, energy bands, density of states, charge density, etc., and realizes the simulation of STM images by integrating the LDOS in certain energy intervals based on the Tersoff-Hamann theory. p4vasp has a user-friendly interface(Fig.2.16), which makes it convenient for researchers to quickly analyze and interpret the results of first principles calculations. p4vasp is a popular and prac-

tical post-processing tool and it is quickly analyze and interpret the results of first principle calculations.

PARCAR is an output file generated by VASP that contains detailed information about the projected wavefunctions and k-point-resolved band structure data. It is primarily used for analyzing orbital projections onto atomic sites and is essential for calculating projected density of states and for performing orbital-resolved band structure analysis. Processing via p4vasp enables the extraction of electronic properties associated with specific atomic sites and orbitals. Due to the large file size, it is typically only explicitly generated when the corresponding flag is set in the VASP INCAR file. Using PARCAR files and p4vasp, we can perform STM simulations and obtain simulated images and parameters.

VESTA

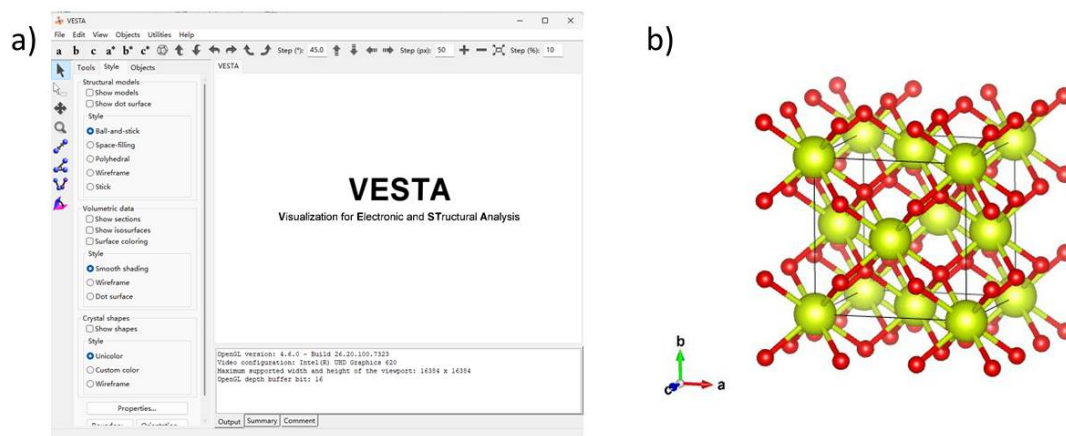


Figure 2.17: a) User Interface of VESTA b) example of the CeO₂ files exported via Vesta.

Visualization for Electronic and Structural Analysis (VESTA) is a powerful 3D visualization software primarily used for analyzing crystal structures, electron density, charge distribution, potential energy distribution, and other related physical quantities. The software was developed by Japanese scientists Koichi Momma and Fujio Izumi[57, 58]. VESTA has become a widely used research tool in materials science, condensed matter physics, computational chemistry, and related fields due to its user-friendly graphical interface, flexible visualization options, and support for multiple file formats. Fig.2.17 is an example of the main interface and display structure.

VESTA supports outputs from major first-principles calculation software, including CIF (Crystallographic Information File), VASP's CHGCAR, ELFCAR, and LOCPOT files, Gaussian's cube files, and WIEN2k's structure and density files. It not only plots precise crystal structures but also generates isosurfaces, color maps, and cross-sectional views from volume data, facilitating intuitive understanding of electronic structures and spatial distribution characteristics. Additionally, it supports unit cell transformations, crystal plane plotting, symmetry operations, defect modeling, crystal slicing, and animation creation, enabling the generation of publication-grade high-quality images.

For crystal structure visualization, VESTA offers extensive options to customize atom colors, radii, bond length displays, periodic boundaries, and atom labels, allowing users to tailor presentation styles to research needs. When handling electron density and charge distribution data, VESTA visually displays the spatial distribution of electrons through isosurface plots and cross-section images. This proves invaluable for studying chemical bonds, bond polarity, van der Waals interactions, and electron localization.

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Chapter 3

Modeling and simulation of the single link on $\text{TiO}_2(110)-(1 \times 2)$ surface

3.1 Chapter description

We conducted a comprehensive investigation of the atomic structure of the link region on the $\text{TiO}_2(110)-(1 \times 2)$ reconstructed surface using a combined approach of scanning tunneling microscopy (STM) and density functional theory (DFT) calculations. Although the $\text{TiO}_2(110)-(1 \times 2)$ surface has long served as a prototypical system for studying surface reconstructions and their influence on catalytic performance, the precise atomic configuration of the link region has remained elusive and subject to ongoing debate. Several structural models have been proposed in the literature; however, none have been conclusively validated by experimental observations.

In this work, we constructed a series of candidate structural models based on the asymmetric (1×2) reconstruction motif and employed the Tersoff–Hamann approximation to simulate STM images for each model. By performing a detailed comparison between simulated and experimentally acquired STM images, alongside formation energy calculations, we were able to critically evaluate the plausibility of each structure. Our analysis reveals a revised atomic model for the link region that reproduces key features observed in high-resolution STM images. This structure provides new insights into the local electronic states and bonding environment of the $\text{TiO}_2(110)-(1 \times 2)$ surface. Moreover, it contributes to a deeper understanding of the reconstruction mechanism and may have implications for surface reactivity and catalytic applications involving rutile TiO_2 .

3.2 Single link on the $\text{TiO}_2(110)-(1 \times 2)$ surface

Titanium dioxide (TiO_2) is an important industrial material with widespread applications in catalysis, purification, and biomedicine[1, 2, 3]. Rutile TiO_2 is the most thermodynamically stable phase, with the (110) surface being particularly stable[4]. Under ultra-high vacuum (UHV) conditions, the $\text{TiO}_2(110)$ surface initially exhibits a (1×1) structure[5]. Through repeated cycles of Ar^+ ion sput-

tering and annealing, the surface undergoes reconstruction to form a (1×2) structure[6]. This reconstruction modifies electronic properties through altered interactions between surface oxygen vacancies and Ti atoms, resulting in adjusted electronic state distributions and enhanced valence band tail formation[7].

These structural modifications lead to improved photocatalytic activity and enhanced reactivity toward water molecules[6, 8]. Consequently, understanding the atomic structure and electronic properties of the (1×2) reconstruction is essential for developing more efficient TiO_2 based catalysts. The $\text{TiO}_2(110)-(1 \times 2)$ surface consists of two distinct regions: the (1×2) region and the link region as shown in the Fig.3.1. The structure of the (1×2) region has been extensively investigated. While initially a symmetric structure was proposed[6], recent studies using density function theory (DFT) calculations[7], scanning probe microscopy (SPM) imaging[9], and transmission electron microscopy (TEM) observations[10] have demonstrated that an asymmetric (1×2) structure is more plausible. Although there has been very little specialized research on the link region, previous studies suggest that the link region is expected to influence catalysis and adsorption on the $\text{TiO}_2(110)-(1 \times 2)$ surface[11, 12], therefore, a detailed analysis of the link region is necessary. The link region is located in the transitional area between adjacent (1×2) strips, with its atomic arrangement different from that of the strip's main body, and it may become a gathering area for oxygen vacancies and active sites. The width of the link region in the $[001]$ direction can be divided into two types. The relatively thick structure is called double link, while the rel-

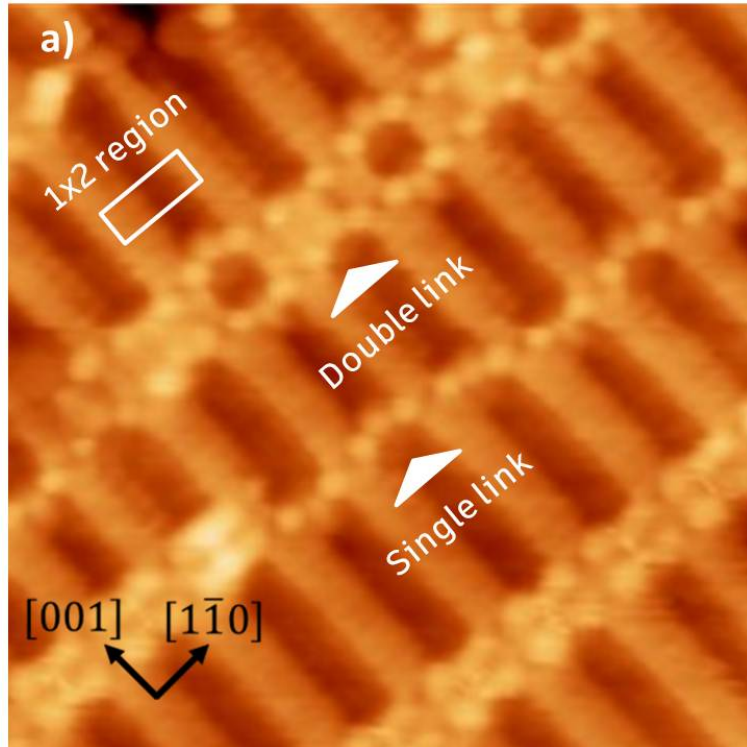


Figure 3.1: STM image of the rutile $\text{TiO}_2(110)-(1 \times 2)$ surface ($10 \text{ nm} \times 10 \text{ nm}$), acquired at a setpoint current $I_t = 100 \text{ pA}$ and a sample bias $V_s = 1.5 \text{ V}$. The image reveals a (1×2) reconstructed region as well as single link and double link structures.

atively thin structure is called single link. Although there is no direct research to prove it, in previous studies, it was often believed that double link is composed of single link[12, 13, 14]. Therefore, the research on the link region should start with a single link. Previous studies have proposed different models for the link structure, including the Ti_3O_6 -added-row model by Bennett et al.[13] and the more widely accepted Ti_2O_3 -added-rows model[14, 12]. However, both models lack definitive experimental verification. Furthermore, considering the asymmetric nature of the (1×2) region, the link structure requires reinvestigation to achieve a more accurate structural model. In recent years, advances in DFT calculations have enabled structural validation through total energy comparisons. However, determining the optimal link structure remains challenging due to uncertainties in the atomic composition and stoichiometry of the link region, making total energy comparisons alone insufficient for structural determination. The Tersoff-Hamann theory[15] provides a complementary approach by enabling simulation of STM images from DFT optimized structures. By directly comparing simulated STM images with experimental observations, the validity of proposed structural models can be more rigorously assessed.

3.3 Experiment

STM measurements were conducted using a custom-built STM system operating under UHV conditions (base pressure $<1.0 \times 10^{-10}$ Torr) at room temperature. Nb-doped (0.05 wt%) rutile $\text{TiO}_2(110)$ single-crystal substrates were employed as samples. Prior to introduction into the UHV chamber, the substrates were ultrasonically cleaned in ethanol to remove organic contaminants and surface impurities.

To obtain the $\text{TiO}_2(110)$ -(1×2) reconstructed surface, the samples underwent repeated cycles of Ar^+ ion sputtering and thermal annealing. Specifically, ion sputtering was carried out using 0.5 keV Ar^+ ions at an Ar partial pressure of 1×10^{-6} Torr, with an ion current of 0.4 μA for 10 minutes. This was followed by annealing at 900 °C under UHV conditions. These treatments effectively transformed the clean $\text{TiO}_2(110)$ -(1×1) surface into the desired (1×2) reconstruction, which is known to exhibit characteristic one-dimensional features along the [001] crystallographic direction.

DFT calculations and STM image simulations were performed to investigate the atomic and electronic structure of the $\text{TiO}_2(110)$ -(1×2) surface. All calculations were carried out using the Vienna Ab initio Simulation Package (VASP)[16, 17]. The projector augmented wave (PAW) method[17, 18] was employed to accurately describe the interaction between core and valence electrons. Exchange-correlation interactions were treated within the generalized gradient approximation (GGA), using the Perdew–Burke–Ernzerhof (PBE) functional[19]. Partial valence (pv) potentials were utilized to include semicore states, such as Ti $3p$ and $3s$ electrons, which are important for describing transition metal oxides.

Geometry optimizations were performed until the residual forces on each atom were below 0.02 eV/Å, ensuring convergence of both atomic positions and total energies. The optimized structures served as the basis for subsequent STM simulations. Simulated STM images were generated using the p4vasp visualization

package (version 0.3.29), based on the Tersoff–Hamann approximation. Simulations were carried out in constant-current mode at a sample bias voltage of +1.5 V, corresponding to the imaging of unoccupied electronic states. Both the structural and electronic information used in the STM simulations were derived directly from the converged DFT results. The simulated images were then compared with experimental STM data to provide insight into the nature of the (1×2) surface reconstruction and the role of Nb doping in modulating the surface electronic structure.

3.4 Initial modeling

3.4.1 Initial modeling of $\text{TiO}_2(110)-(1 \times 2)$

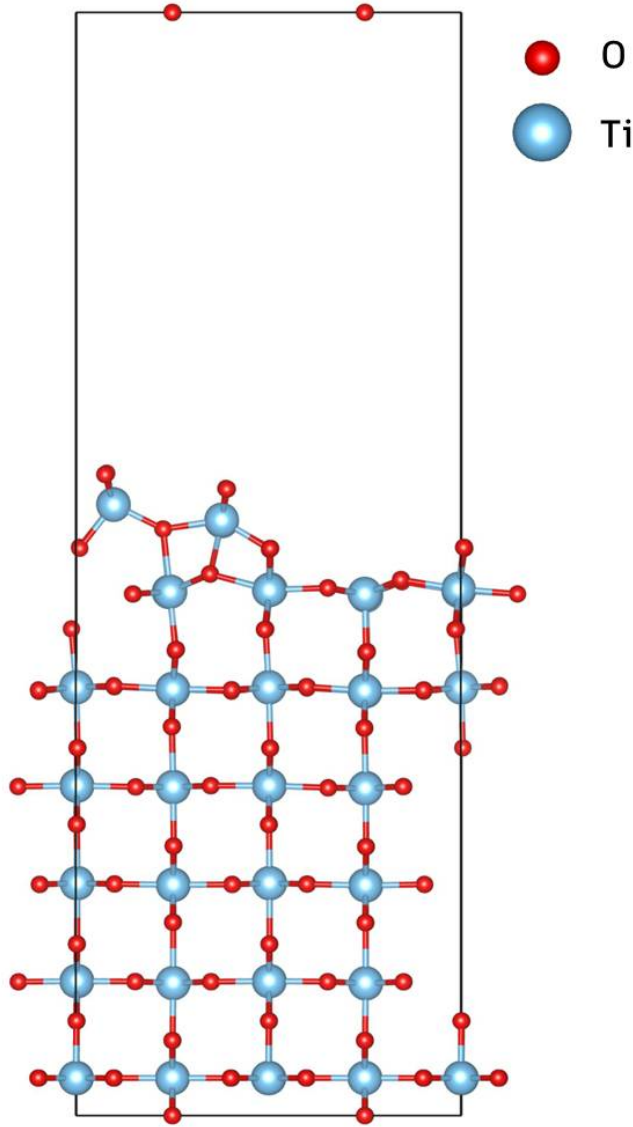


Figure 3.2: Ball-stick modeling of the $\text{TiO}_2(110)-(1 \times 2)$ structure without link structure. Red represents oxygen atoms and blue represents titanium atoms.

The $\text{TiO}_2(110)$ surface structure can be divided into two parts: the (1×2) region

with band reconfiguration and the adjacent link region. Since the structure of the (1×2) region has been thoroughly discussed in previous studies, this research first optimizes the model for this part while retaining the position of the link region. To improve the computational efficiency while ensuring accuracy, the basic model is systematically optimized, providing a reliable structural basis for subsequent first-principles calculations and STM simulations.

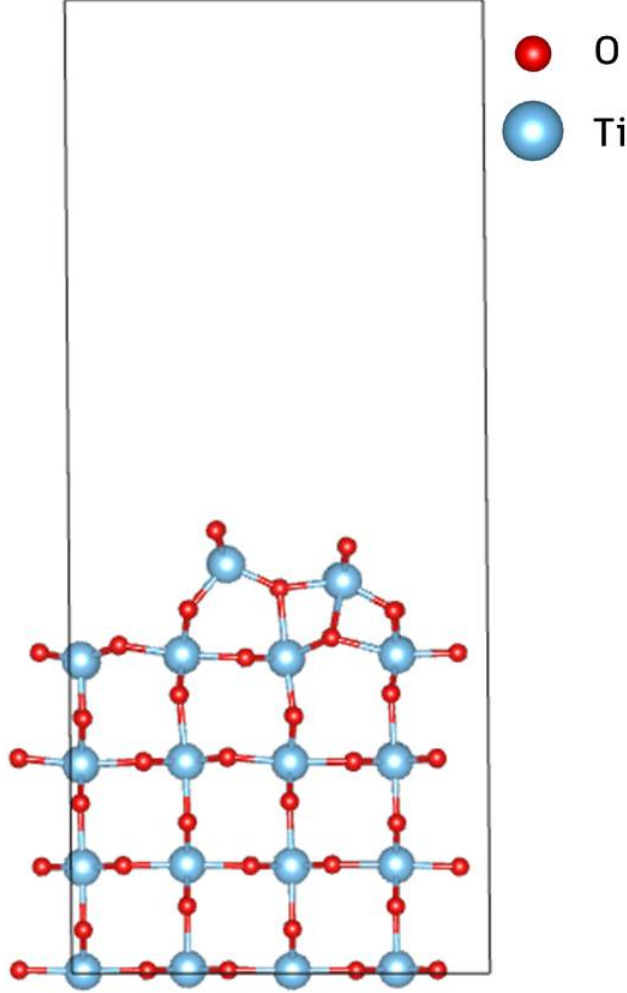


Figure 3.3: Ball-stick modeling of the $\text{TiO}_2(110)-(1 \times 2)$ structure without link structure after simplified. Red represents oxygen atoms and blue represents titanium atoms.

As shown in Fig.3.2, the asymmetric Ti_2O_3 model, without the inclusion of a link structure, is currently the most widely accepted reconstruction for the $\text{TiO}_2(110)-(1 \times 2)$ surface. This model has been extensively validated through various experimental and theoretical techniques, including scanning probe microscopy (SPM)[9], density functional theory (DFT) calculations[7, 20], and scanning transmission electron microscopy (STEM)[10]. In this work, our structural model is based on the Ti_2O_3 framework recently proposed by Yuan Wentao et al[10] which we further optimized using the VASP package under our specific computational parameters. Since the primary objective of this study is to investigate the surface structure, the structural optimization was carried out with a focus on balancing computational

efficiency and accuracy. This strategy enables us to reduce computational time while maintaining a reliable and representative model that meets our research requirements.

Given the large size and high atom count of the original model, simplification was necessary prior to optimization. Based on previous studies of TiO_2 , it is generally accepted that retaining four to five atomic layers sufficiently preserves the surface composition and properties without significantly affecting the overall structure. Accordingly, the initial model used in this work, as depicted in Fig.3.3, includes five layers in total.

To further improve computational efficiency and focus on surface structural changes, the atoms in the bottom layers were fixed during optimization. Additionally, oxygen and hydrogen atoms were not included at the bottom of the slab model to simplify the system while maintaining surface accuracy. Therefore, we selected Fig.3.3 as the preliminary initial model for calculation. According to the conclusions of relevant papers on TiO_2 calculations, a four to five layers structure is sufficient to support the calculation while ignoring the influence of the number of layers[21, 22]. At the same time, the length in the z direction was shortened to increase the calculation speed. The parameters for other parts will be confirmed step by step.

3.4.2 Parameters and calculation models improvement

To rigorously evaluate the validity of the proposed optimization model and to systematically determine appropriate parameter settings, two controlled defects were deliberately introduced into the most critical region of the surface structure prior to optimization, as illustrated in Fig.3.4-a). These intentional perturbations serve as a diagnostic tool to probe the sensitivity of the model to structural imperfections and to facilitate a more transparent assessment of the model's ability to restore or preserve the ideal surface configuration under varying conditions. By comparing the optimization outcomes obtained under two distinct sets of parameters, shown in Fig.3.4-b) and Fig.3.4-c), we are able to evaluate model performance.

In both test cases, the artificially introduced defects were successfully corrected by the optimization process. However, the results presented in Fig.3.4-c) exhibit noticeable instability and a reduction in overall optimization quality compared to Fig.3.4-b). Our primary objective is to enhance the accuracy of surface structure optimization while maintaining reasonable computational cost. To this end, we tuned the optimization parameters to achieve results comparable to those shown in Fig.3.4-b), where all deviations between the corrected atomic positions and their expected ideal locations are no visible error. In order to make the research more accurate, we conducted further comparisons as shown in Fig.3.5.

Under different parameters, we further analyzed the reliability of the calculation results by conducting statistical analysis of the coordinates. We separately recorded the x position before the movement and the x position after the movement, and calculated the difference, which is the error value of this optimization. At the same time, the time required for this optimization is recorded as a reference data. As can be seen, when $\text{EDIFFG} = -0.5$, the errors of the two reserved atoms are both around $0.05 \text{ \AA}$. As this value decreases to -0.1 , the error of the y atom significantly reduces. And when this value is lower than -0.05 , the overall error

a) Pre-optimization

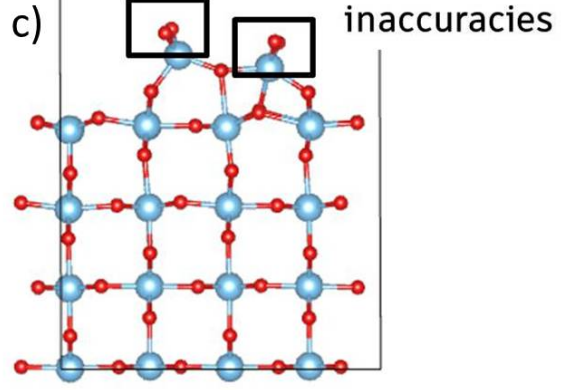
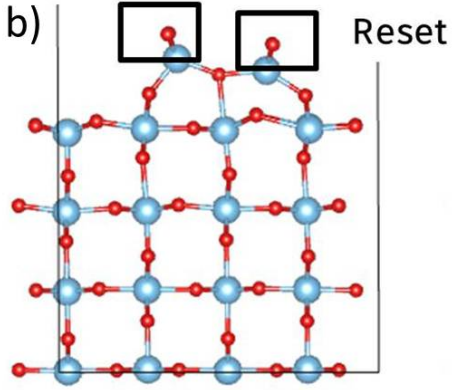
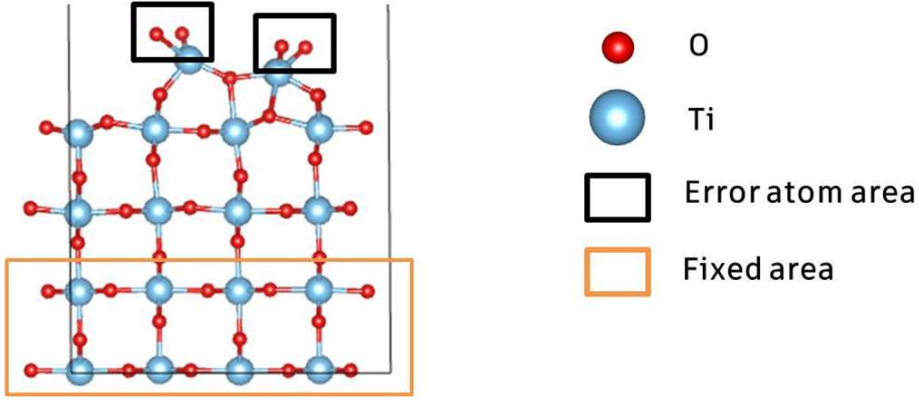


Figure 3.4: Ball-stick modeling of the $\text{TiO}_2(110)-(1 \times 2)$ structure without link structure after simplified. Red represents oxygen atoms and blue represents titanium atoms. The black areas are reserved errors and the orange areas are fixed atom sections. a) is the structure before optimization, b), c) are the structures after optimization with different parameters.

is less than $0.005 \text{ \AA}$. In first-principles calculations, it is generally considered that an error of around $0.05 \text{ \AA}$ is an acceptable value [23, 24]. Taking into account the computing speed and the fact that the final optimization result will be relatively large, $\text{EDIFFG} = -0.5$ is an acceptable parameter. During the subsequent model optimization process, we will also apply this standard for verification.

This level of precision ensures a physically meaningful reconstruction while avoiding overfitting or excessive resource usage. The main parameters governing the optimization are set as $\text{EDIFF} = 5.0\text{e-}06$ and $\text{EDIFFG} = -0.5$, which define the electronic and ionic convergence criteria, respectively. Given the relatively large number of atoms involved in the surface model, these thresholds offer a reasonable compromise between convergence speed and structural accuracy. The values fall well within the acceptable range for systems of this scale, ensuring consistent and reproducible outcomes. A comprehensive list of the optimization parameters, including cut off energies, k-point sampling, and convergence criteria, is provided in the Appendix for reproducibility and further reference.

To further enhance computational efficiency, we adopt a strategy of selectively

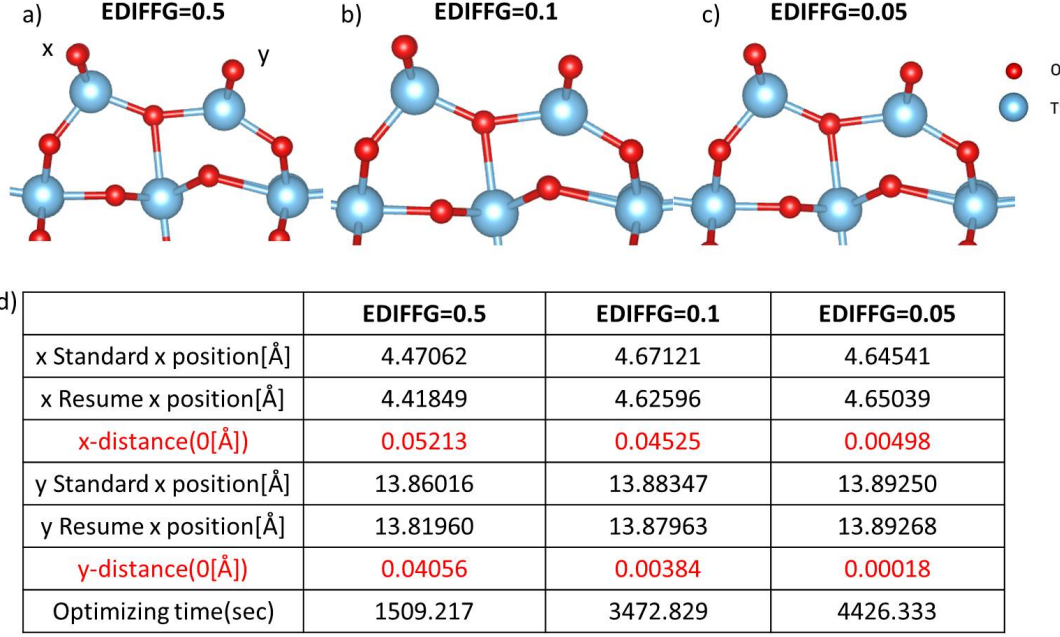


Figure 3.5: Optimized structures under different parameters all have no visible errors. a), b), c) represent the optimization results under the conditions of EDIFFG = -0.5, -0.1, -0.05 respectively. d) shows the response of the reserved error atoms. In the table, it presents the optimized positions and the original positions of two different reserved atoms in the x-direction, along with the differences. The last row of the table is the time used for this optimization.

immobilizing the deeper atomic layers while allowing full relaxation of the surface atoms. This approach aims to reduce the degrees of freedom during optimization without compromising the accuracy of the surface reconstruction. The key objective is to isolate and preserve the relevant structural changes occurring at the surface, which are the primary focus of this study. Fig.3.6 provides a comparative analysis of optimization results under different fixed-layer configurations. Fig.3.6-a) shows the initial, pre-optimization structure, in which all atoms are using the previously defined parameter set. The initial model of this structure serves as the optimized reference model and benchmark for subsequent optimization.

Fig.3.6-b) to Fig.3.6-e) present the optimized structures under four different fixed-layer configurations, corresponding to cases where three, two, one, and zero bottom atomic layers are constrained, respectively. Notably, in Fig.3.6-e)—where no atoms are fixed, and the optimized structure exhibits slight distortions at the bottom region. This deformation is primarily attributed to unbalanced residual stress arising from the absence of terminating species, such as hydrogen or oxygen atoms, which would otherwise passivate the bottom surface and compensate for the surface dipole or lattice mismatch. Despite this distortion, the main focus of this study is the surface structure, remains intact and stable, indicating that the bottom layer deformation has negligible influence on the physical or chemical behavior at the surface. These results suggest that fixing a max number of bottom layers can effectively suppress artificial deformation in the bulk-like region while preserving accurate modeling of the surface phenomena.

As seen in Fig.3.6-b) to Fig.3.6-d), fixing up to three bottom layers leads to no sig-

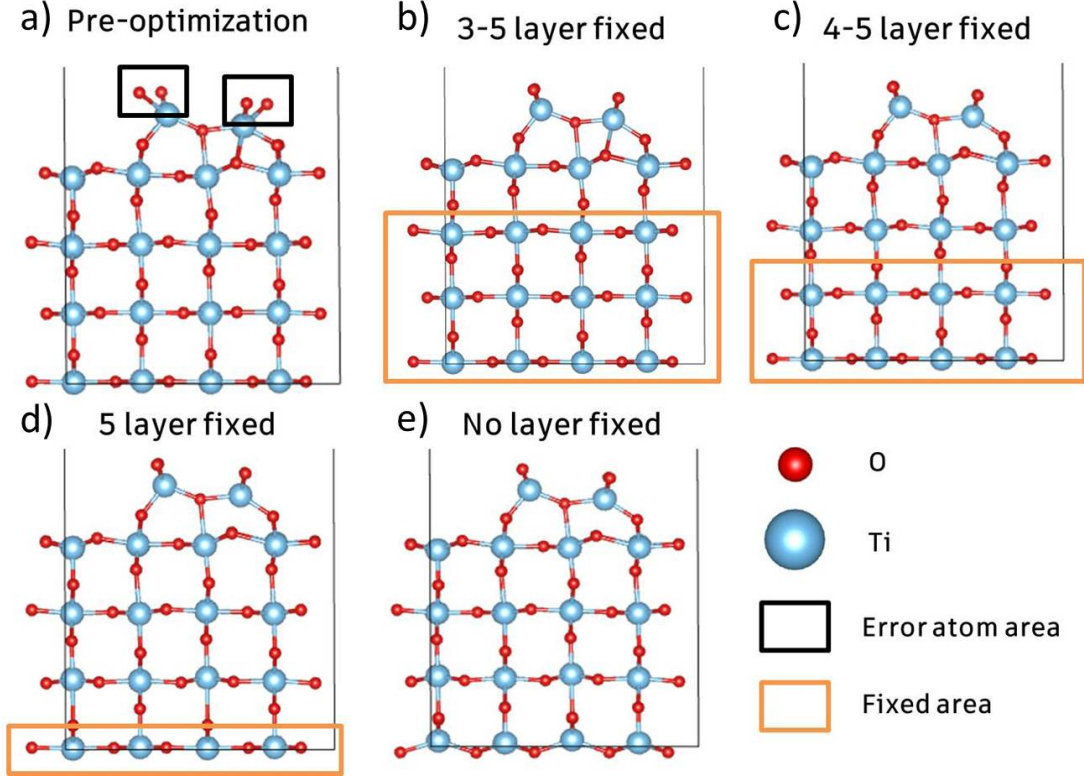


Figure 3.6: Ball-stick modeling of the $\text{TiO}_2(110)-(1 \times 2)$ structure without link structure after simplified. Red represents oxygen atoms and blue represents titanium atoms. The black areas are reserved errors and the orange areas are fixed atom sections. a) is the pre-optimization structure b), c), d) and e) show the after optimizing results for fixed three-layer atoms, two-layer atoms, one-layer atoms and unfixed atoms, respectively.

nificant differences in the surface optimization results. Since our analysis is limited to surface structural changes, and does not involve deeper atomic rearrangements, fixing the bottom three layers offers an optimal balance between computational efficiency and structural fidelity. Accordingly, we adopt this configuration, that fixing the bottom three atomic layers, as the default setup in all subsequent optimization calculations.

To investigate the surface link structure in greater detail, the final supercell is expanded in the xy-plane. This expansion substantially increases the number of atoms in the system, leading to significantly longer computation times. To mitigate this, we aim to reduce the total number of atoms wherever possible, including within the fixed layers, while preserving the structural integrity and accuracy of the surface region. The optimization process associated with this step is illustrated in Fig.3.7.

Fig.3.7-a) presents the structure prior to optimization. Following the methodology established in earlier steps, intentional errors are introduced into the surface to evaluate the stability of the model. The same set of parameters and fixed-layer configuration (i.e., fixing to the third layer) is maintained throughout. Fig.3.7-b) to Fig.3.7-d) show the optimized structures for systems containing five, four, and three atomic layers in total, respectively.

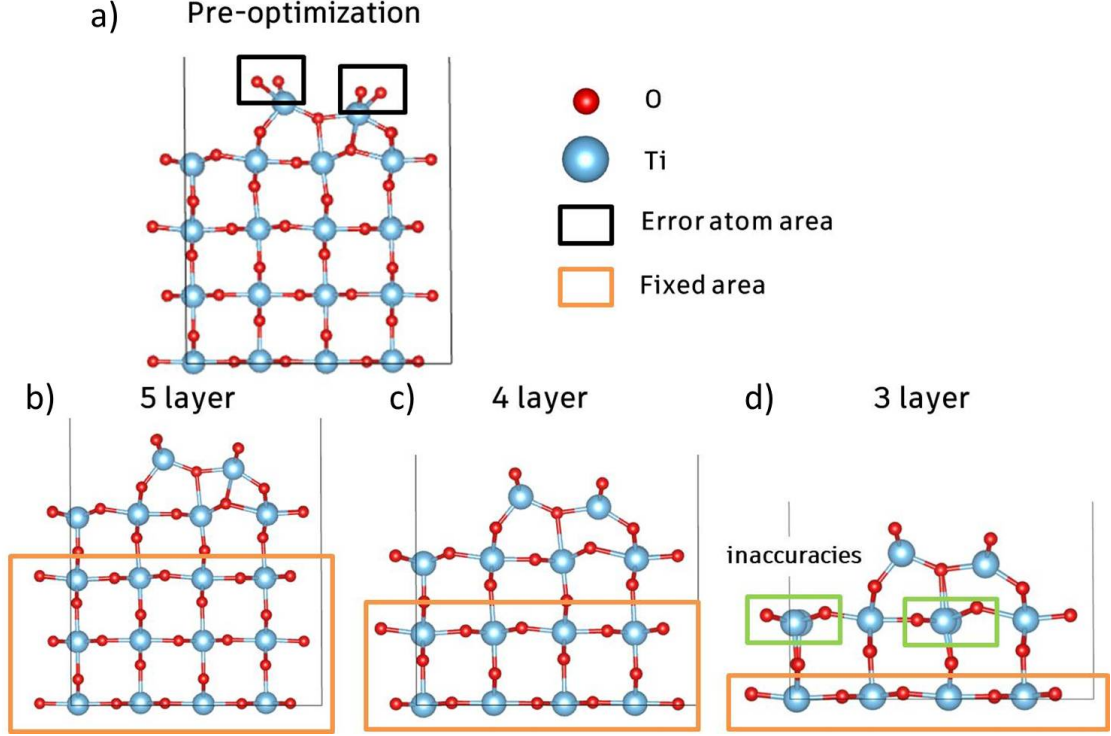


Figure 3.7: Ball-stick modeling of the $\text{TiO}_2(110)-(1 \times 2)$ structure without link structure after simplified. Red represents oxygen atoms and blue represents titanium atoms. The black areas are reserved errors and the orange areas are fixed atom sections. a) is the pre-optimization structure b), c) and d) show the after optimizing results for five-layer case, four-layer case and three-layer case, respectively.

The results indicate that the surface structures obtained in the five-layer and four-layer models remain virtually identical after optimization, confirming that the surface features are well preserved under both configurations. However, in the three-layer model (Fig.3.7-d), noticeable misalignment appears in the second atomic layer, suggesting that excessive reduction of the system size begins to compromise the reliability of surface reconstruction.

Based on these observations, the four-layer configuration is selected for subsequent calculations. This choice represents an optimal trade-off between computational efficiency and structural fidelity, ensuring that the surface behavior remains accurate without incurring unnecessary computational cost.

3.4.3 Supercell of the model

As shown in Fig.3.8, through the STM image, we can get more information of the single link structure. The single link has two opposite orientations along $[001]$, which are symmetrical along $[1\bar{1}0]$. Therefore, sufficient length must be reserved to verify that the direction matches the actual situation. The single link exists between two (1×2) columns and consists of roughly three equal-sized highlights. From line profile along the $[1\bar{1}0]$, due to the asymmetry of the (1×2) structure, the single link may have a small height difference between the left and right side,

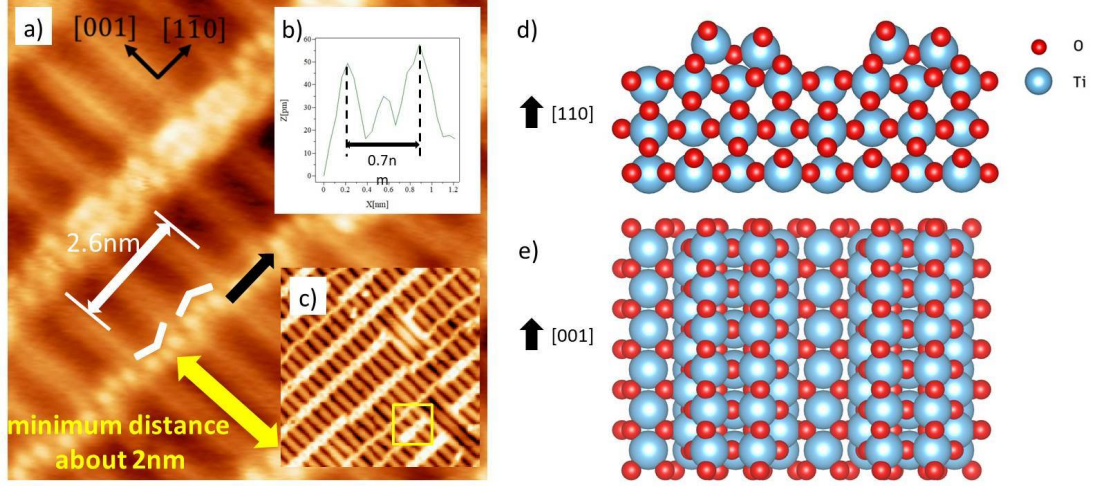


Figure 3.8: a) STM image ($10 \text{ nm} \times 10 \text{ nm}$) of the rutile $\text{TiO}_2(110)-(1 \times 2)$ surface, $I_t = 100 \text{ pA}$ and $V_s = 2.0 \text{ V}$. Along the $[001]$, the single link has two opposite orientations, and the minimum spacing between the links is about 2 nm . along the $[1\bar{1}0]$, the distance between the (1×2) columns is 1.3 nm , and the distance between the two bright dots is roughly 0.7 nm as shown by the line profile. b) line profile on STM image shown in a). c) STM image ($20 \text{ nm} \times 20 \text{ nm}$) of the minimum distance between links. d) the side view of the basic model of the $\text{TiO}_2(110)-(1 \times 2)$ surface, e) the top view of the basic model of the $\text{TiO}_2(110)-(1 \times 2)$ surface.

which has roughly 0.7 nm spacing. In a large number of STM images, there is no fixed value for the spacing between links. However, by comparing a large number of images, the minimum spacing between the links is about 2 nm along the $[1\bar{1}0]$. Therefore, the spacing between links must be at least greater than the minimum value. The final model was constructed as a $2 \times 6 \times 1$ supercell containing 492 atoms, with dimensions of approximately $a = 1.8 \text{ nm}$, $b = 2.6 \text{ nm}$, and $c = 2.7 \text{ nm}$. This supercell size was chosen to adequately represent the surface reconstruction while maintaining computational efficiency.

The final atomic configuration used for surface optimization consists of a four-layer structure, with the bottom two layers fixed to simulate bulk constraints. To construct a realistic surface link structure, it is necessary to expand this base unit into a supercell. The model is first doubled in the direction perpendicular to the (1×2) surface reconstruction to allow for the formation of inter unit linkages. Subsequently, the structure is extended along the direction parallel to the (1×2) reconstruction to a total length of approximately 2 nm , corresponding to the minimum observed link spacing. Based on these geometric and experimental considerations, a supercell is constructed, and structural optimization is carried out.

The optimization process utilizes the previously established four-layer slab configuration, with the bottom two layers fixed throughout the relaxation. Fig.3.9-a) shows the pre-optimization structure. To assess the reliability of the optimization model under non-ideal conditions, a series of intentional perturbations are introduced. Specifically, atoms in various layers and positions are displaced from their equilibrium coordinates. Within the fixed region, one atom is selectively freed to introduce a controlled degree of variability, simulating minor deviations that

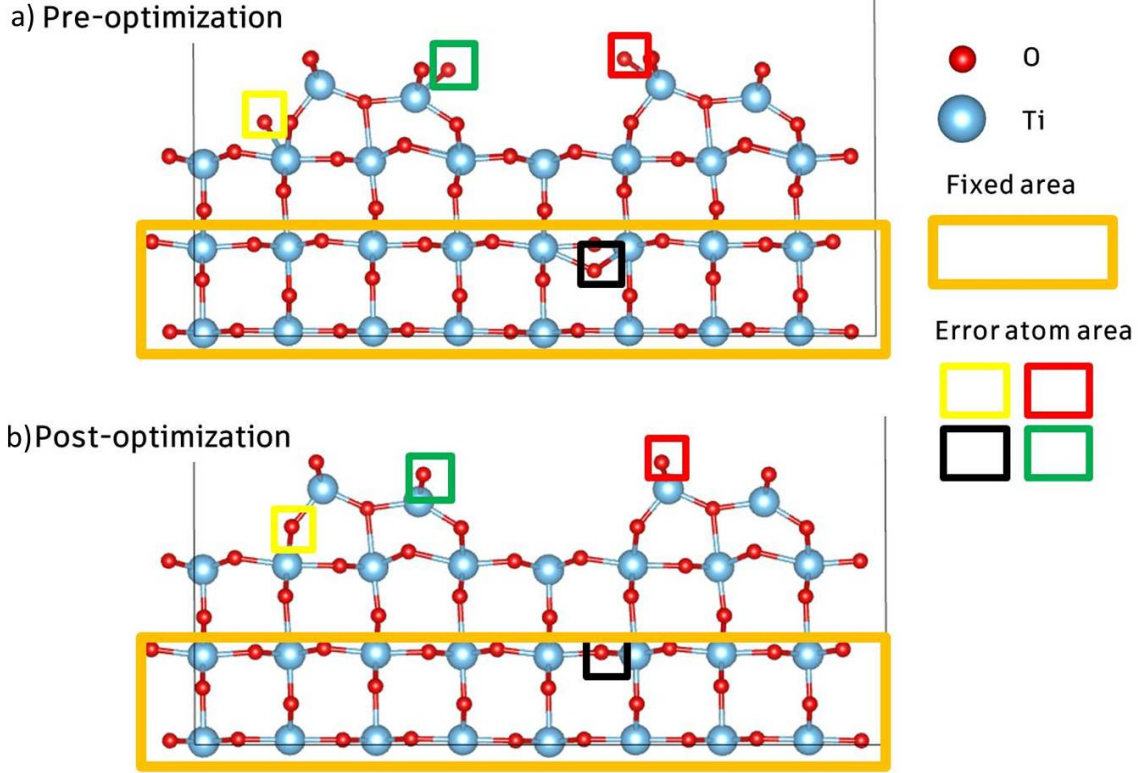


Figure 3.9: Ball-stick modeling of supercell of the $\text{TiO}_2(110)-(1 \times 2)$ structure without link structure with $a = 1.8 \text{ nm}$, $b = 2.6 \text{ nm}$, and $c = 2.7 \text{ nm}$. Yellow, red, black and green respectively represent the different error areas reserved. The bottom two layers represented by the orange area are fixed. In the fixed area, select one movable atom and set it as the incorrect atom. a) This is the structure before optimization, b) This is the structure after optimization.

could arise from imperfect boundary conditions. In the upper layers, additional positional shifts are applied to mimic potential deviations introduced by adjacent features.

The post-optimization result is presented in Fig.3.9-b). After structural relaxation, all atoms that were initially displaced return to their expected lattice positions, and the overall geometry exhibits no signs of significant distortion or instability. These results confirm the robustness and structural integrity of the optimization approach, even under perturbed initial conditions. Consequently, the resulting supercell is adopted as the base configuration for the subsequent construction and analysis of the surface link structure. Its stability, consistency, and agreement with experimental observations ensure that it provides a reliable foundation for further simulation and interpretation.

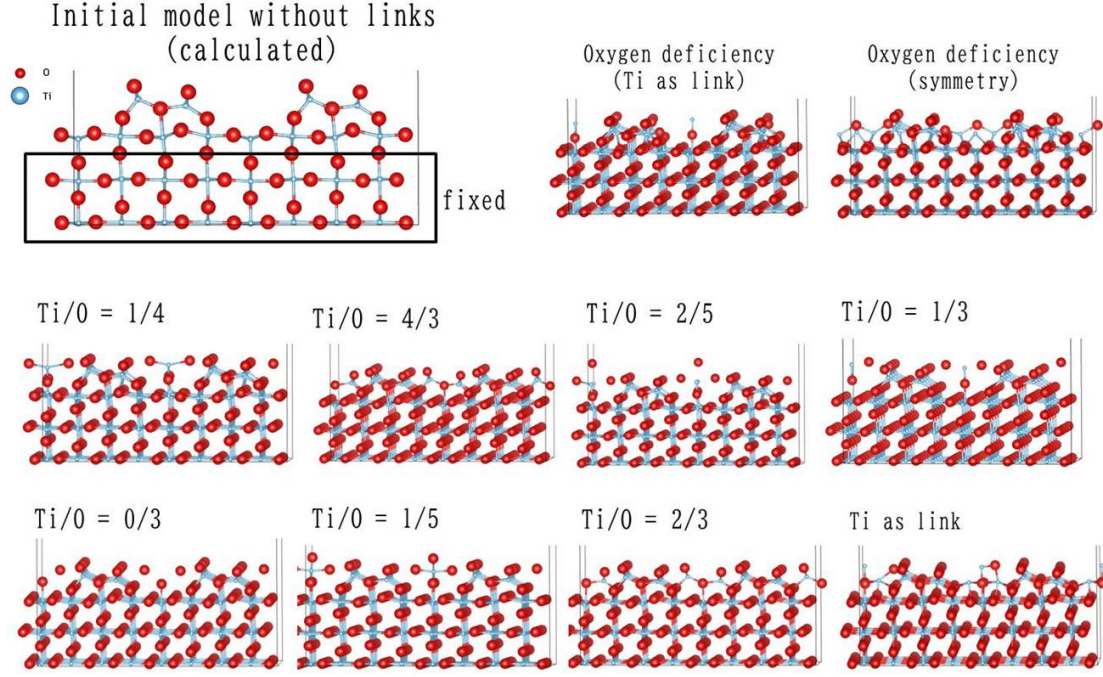


Figure 3.10: Schematic diagrams of some models we considered: The top-left shows the original model schematic, the bottom two atomic layers are fixed. While the other smaller models represent pre-optimization versions, including model with different ratios of titanium atoms to oxygen atoms, oxygen-deficient model and model featuring Ti as a highlight.

3.5 Modeling and simulation

3.5.1 Modeling

Total modeling

Building upon prior research, we proposed a series of surface structure models to further elucidate the atomic arrangement of the $\text{TiO}_2(110)-(1 \times 2)$ reconstructed surface. To mitigate potential artifacts introduced by minor asymmetries or local distortions, we systematically constructed multiple models varying in atomic configurations and stoichiometry, all based on the well-established Ti_2O_3 -added-rows model. These variations were designed to account for different structural scenarios that may arise under experimental conditions.

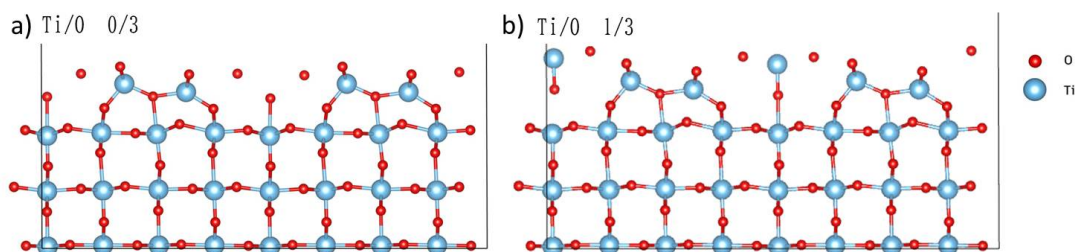
In parallel, we incorporated high-resolution STM images alongside supplementary experimental observations to refine and expand our structural hypotheses. Based on this comprehensive approach, we proposed several additional candidate models, as illustrated in Fig.3.10. The figure presents selected optimized structures, including modified versions of the Ti_2O_3 -added-rows model, oxygen-deficient configurations, and a more unconventional model incorporating externally bonded Ti atoms.

These models were generated by systematically adjusting key parameters such as the initial atomic positions, the oxygen to titanium atomic ratio, and plausible surface rearrangements. Each structure underwent full relaxation using DFT to

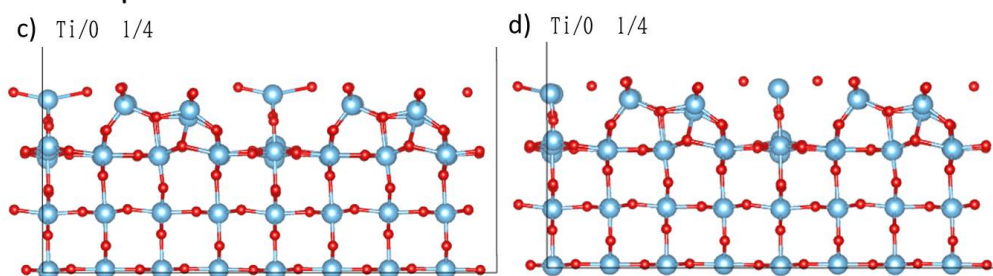
obtain its energetically favorable configuration. Subsequently, STM simulations were performed for all models using the Tersoff–Hamann approximation, enabling direct comparison with experimental STM images.

Model factors

Increase or decrease the number of atoms



Initial position



Models with different approaches

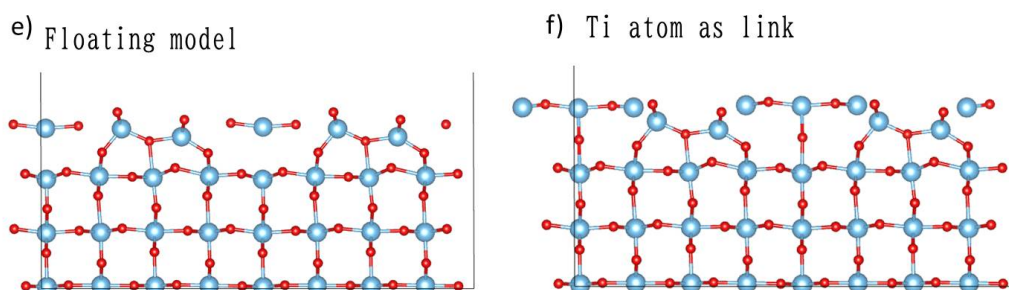


Figure 3.11: Ball-stick modeling before optimizing of the a) ,that there is no Ti in the middle of the link structure. b) that there is a Ti in the middle of the link structure. c) d), that there are slight differences in the positions of Ti in the middle, which leads to changes in chemical bonds. e),which is a floating model without atoms in the second layer in the link region. f), that it uses Ti out of the position as the bright bot position.

In the process of model construction, this study comprehensively considered various factors to ensure that the simulation results have representativeness and credibility within a broader scope. Firstly, different numbers and proportions of atoms would directly affect the overall chemical composition and local environment of the system, thereby changing the structural stability, energy distribution, and possible reaction pathways, therefore, we systematically adjusted these parameters in the model to evaluate the impact of composition changes on the properties of the

system(Fig.3.11-a)-b)). It is precisely for this reason that makes the subsequent comparison even more complicated. Secondly, the initial positions of atoms play a crucial role in the energy convergence path, local configuration, and the final stable structure obtained. Different initial configurations may lead the system to fall into different energy minima, so diverse initial arrangements must be made to avoid configuration bias. As shown in fig.3.11-c)-d), different minor positional differences led to changes in the chemical bonds when the structure diagram was exported. During the actual process of optimizing the structure, atoms that have not formed chemical bonds are prone to disperse and separate from the overall structure. Therefore, when considering various structures, it is often necessary to adjust the initial position of the same model and perform repeated calculations to obtain the most reasonable result. Moreover, special model structures may potentially form effective link structures, which are therefore included in the model consideration to cover the possible structural features. For instance, there is the less likely floating model. Although this model fails to yield the desired results, its change process can provide ideas for thinking about other models. For another example, we removed the Ti atoms and hoped to form a structure with three bright spots at a higher position. However, the optimization result of this model disrupted the overall structure, significantly reducing the scope of the model under consideration. By comprehensively considering these factors, the model can more comprehensively cover the diversity of the system and ensure that the obtained results have higher reliability in mechanism understanding and property prediction.

3.5.2 Simulation

Due to the variation in the total number of atoms across the different structural configurations, a direct comparison of total energies is not meaningful in this context. To address this limitation, we employed a structure validation strategy based on simulated STM images. Specifically, STM simulations were performed using the Tersoff–Hamann method, which allows for a qualitative and semi-quantitative comparison between the calculated local density of states (LDOS) and experimentally acquired STM topographies. The reliability of each model was assessed by evaluating the level of agreement between the simulated and experimental STM images. To identify the most plausible structure, we systematically explored approximately 50 different configurations, generated by varying the oxygen to titanium ratios, initial atomic positions, and surface arrangements. All models were fully relaxed using DFT calculations via the VASP, followed by STM image simulations.

Significant error

Many of these trial models exhibited unphysical or unstable features, such as severe distortions of the (1×2) stripe pattern or partial structural dissociation and a clear conflict with the STM image. As shown in Fig.3.12, this figure displays the optimization results based on the Ti_2O_3 -added-rows model and the STM simulated image. These models adjust the ratio of Ti atom to O atom and continuously refine the initial positions to achieve better results. These models can still

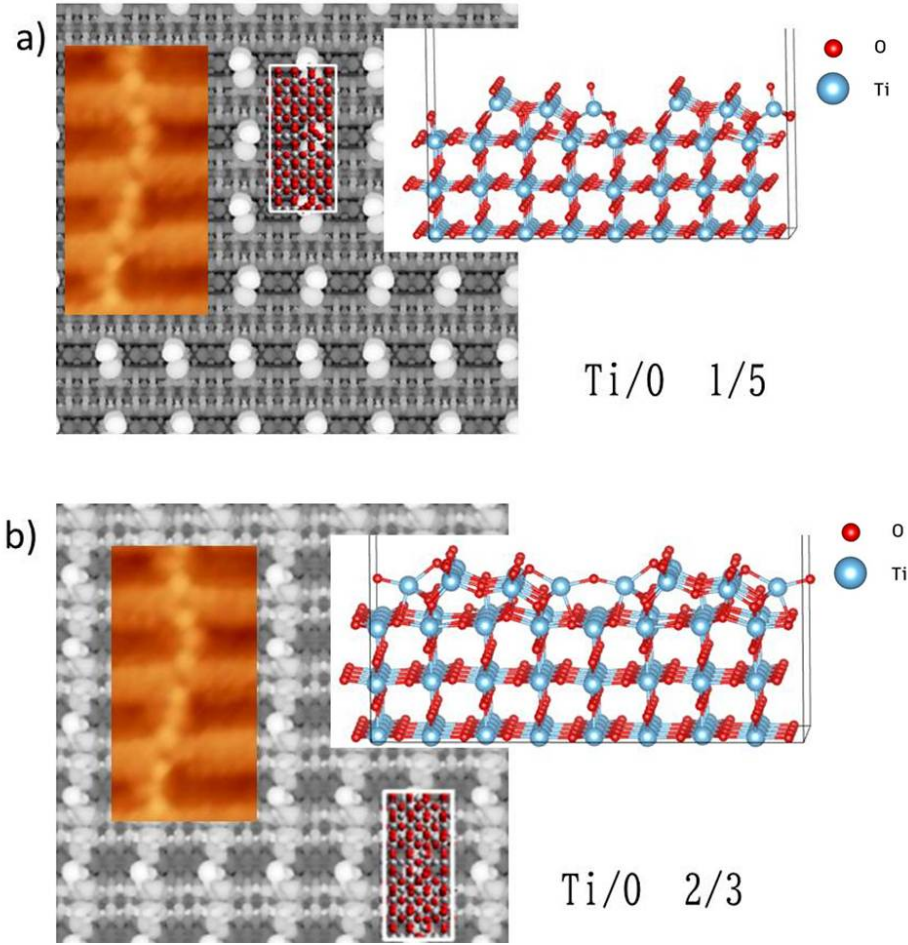


Figure 3.12: Ball-stick modeling and STM simulation images and its actual images of the a) the ratio of Ti to O is 1 to 5 in the link region. b) the ratio of Ti to O is 2 to 3 in the link region. The STM image inside the simulation image is the actual STM image.

be deemed unreasonable without requiring detailed comparisons to actual STM images. While the (1×2) regions of the simulated image and the actual image can align, the features in the link region are significantly mismatched. Although three bright spot features are present, their overall relative positions fall far short of expectations, and the sizes of the bright spots also deviate from the anticipated. Fig.3.13 illustrates another status. The simulation results reveal that Fig.3.13-a) depicts a model with additional Ti atoms, where the optimized structure causes dissociation in the (1×2) region. Fig.3.13-b) shows a different case: due to adjustments in the initial positions and the number of atoms in the (1×2) region, the link portion has completely lost its characteristic features. These situations are completely different from actual STM images.

Acceptable (retained) model

We have set the following criteria for the selection of the simulated images. Firstly, based on the characteristics of the actual STM images, the selected simulated images should present a complete (1×2) structure, have a clearly distinguishable link configuration, exhibit the typical features of three bright spots, and have the

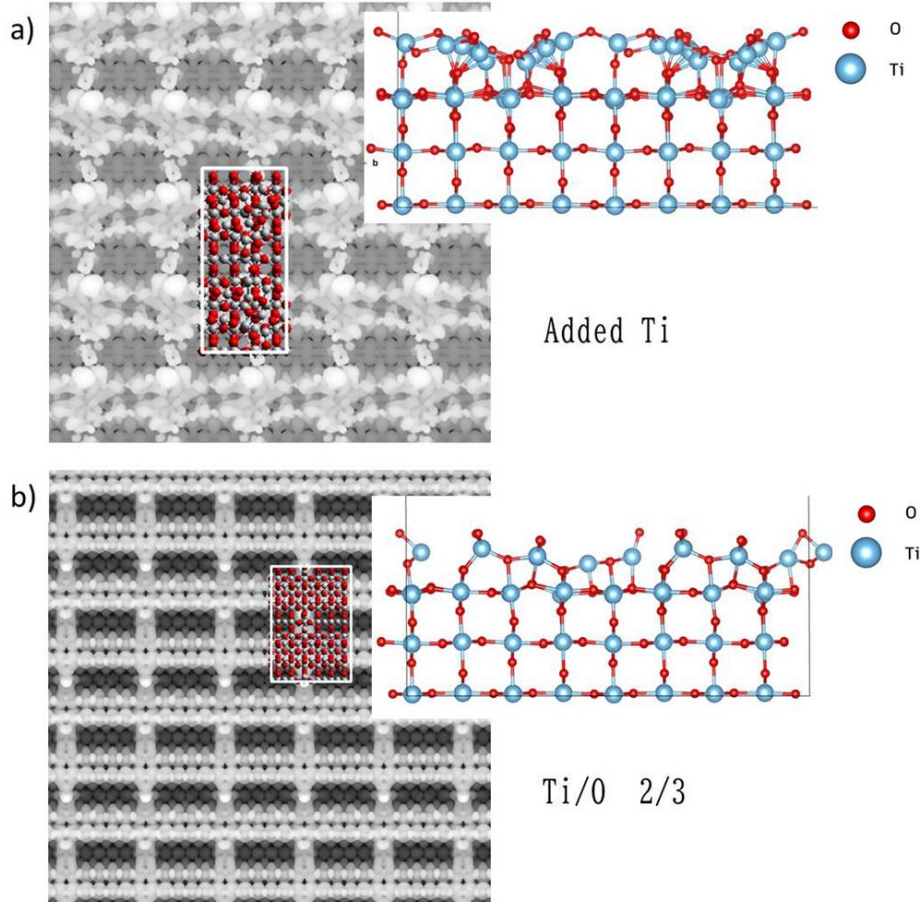


Figure 3.13: Ball-stick modeling and STM simulation images of the a) the added Ti model, and b) the ratio of Ti to O is 2 to 3 in the link region.

possibility of having a symmetrical atomic structure after optimization. Secondly, in terms of the overall geometric proportion, the simulation results should be basically consistent with the experimental characteristics of the link structure, with the long side spacing approximately 0.7 nm and the short side spacing approximately 0.3 nm.

Among the different modeling, there is an oxygen-deficient model. This model is a more simplified version. The oxygen atoms in the (1×2) columns are removed, forming a simple structure in the link region between the columns. This model structure is self-proposed based on the image and structural characteristics of STM. As shown in Fig.3.14, after multiple structural optimizations, this diagram presents three models yielding comparable simulated images. The three models share the same (1×2) column structure, but their link regions contain one titanium atom, one oxygen atom, and two titanium atoms with one oxygen atom, respectively (Fig.3.14-a),b),c)). The simulated images ultimately produced closely resemble the structure of the three bright spots. However, actual STM images reveal that the three bright spots are nearly identical in size, with no significant height differences between them. The effects demonstrated by b and c are clearly inconsistent. Regarding the structure of Fig.3.14-a), we consider it suboptimal in terms of presenting symmetry and in comparison with subsequent models. These discrepancies indicate that many of the trial structures, despite be-

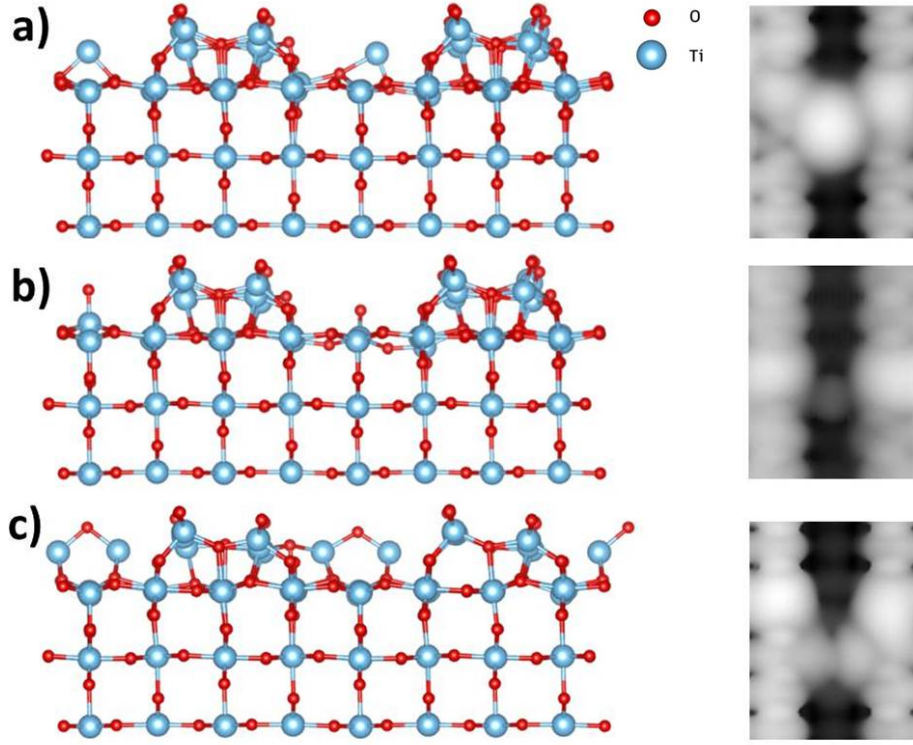


Figure 3.14: Several relatively similar typical models. Side view and STM simulation of a) OD-Ti-OD model, b) OD-O-OD model, c) OD-2Ti1O-OD model.

ing energetically optimized, do not accurately capture the essential characteristics of the reconstructed surface.

Most reasonable model

In addition to the several typical structures, we also made minor adjustments to different structures for comparison. After comprehensively comparing all structures and simulations, although some simulated structures also resemble the link structure, considering the structural characteristics of the link, the structure that reproduces three approximately equal bright spots. Its overall configuration is fundamentally consistent with the Ti_2O_3 -added-rows model. We further optimized this structure under asymmetric (1×2) conditions, and the results are also shown in Fig.3.15. The central position of this model is Ti_2O_3 -added-rows model, where one oxygen atom is removed from the (1×2) region to maintain overall balance. By altering the position of the central structure, it can be transformed into a single link symmetric structure along [001]. It retains the complete 1×2 region of the actual STM image display and the clear link image, with three bright spots and the possibility of symmetry. This is the model we believe to be closest to the correct structure based on extensive simulations.

The distance between the bright spots on the left and right sides is 0.65 nm. This data is basically consistent with the 0.7 nm obtained from STM. Considering that the local electron density may not be entirely above the Ti atoms, the difference is also acceptable. Meanwhile, this structure possesses a symmetrical structure

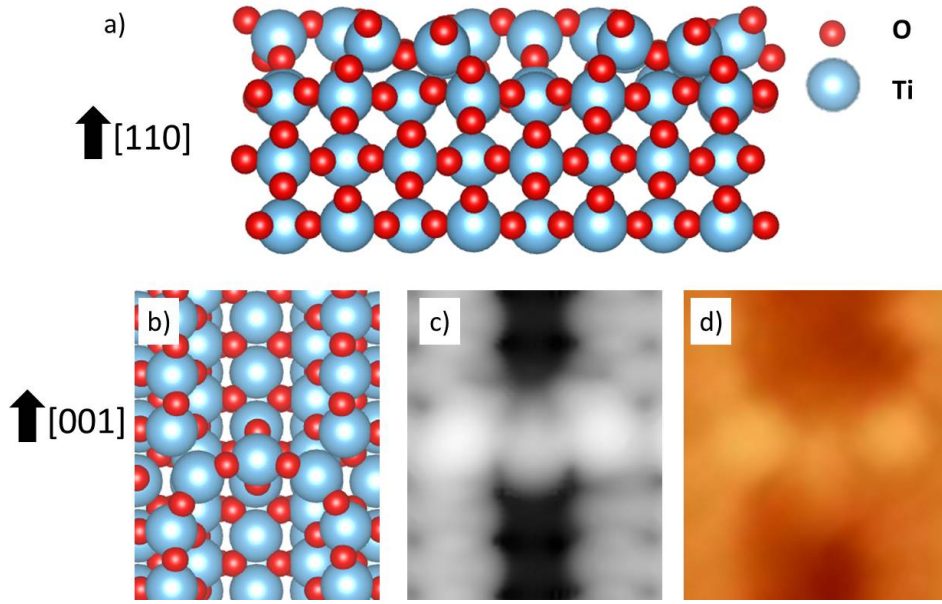


Figure 3.15: Modeling after optimize, a) is the side view of the model(space-filling model), b) is link part the top view of the model, c) is the STM simulation of the model, d) is the STM image of single link.

in the $[001]$ direction, which conforms to the characteristics of the STM images. Although the simulated image of STM is slightly different from the actual image, considering the actual situation where factors such as probe state and noise cause changes in clarity, and there may be some deviations during the simulation process, this image can be regarded as a reproduction of the actual image.

In order to demonstrate another crucial feature of single link, that single link structures exhibit opposite orientations along the $[001]$ direction. We calculated the total energy to further verify the rationality of the model. The structures of the single link in the same direction $[001]$ and the single link in the opposite direction $[001]$ are different only in their structures. The number and proportion of atoms are exactly the same in both. Therefore, this was verified by directly comparing the total energies. The optimized model and results are shown in Fig.3.16. We obtained detailed information of the two structures. The results shown in Fig.3.16 indicate that the configuration with alternating orientation has a lower total energy, with the total energy being about 0.6 eV lower. The 0.6 eV free energy difference reflects a clear thermodynamic superiority or inferiority relationship between the two states. This will result in a difference of order of magnitude in their occurrence probabilities, which means that the arrangement with opposite directions is more advantageous in terms of total energy and also more stable in structure. This difference represents that the disadvantageous model is almost impossible to occur[25, 26], which is consistent with the conclusion we obtained from the STM observation, that is, in large-area images, the single link always appears in the opposite orientation.

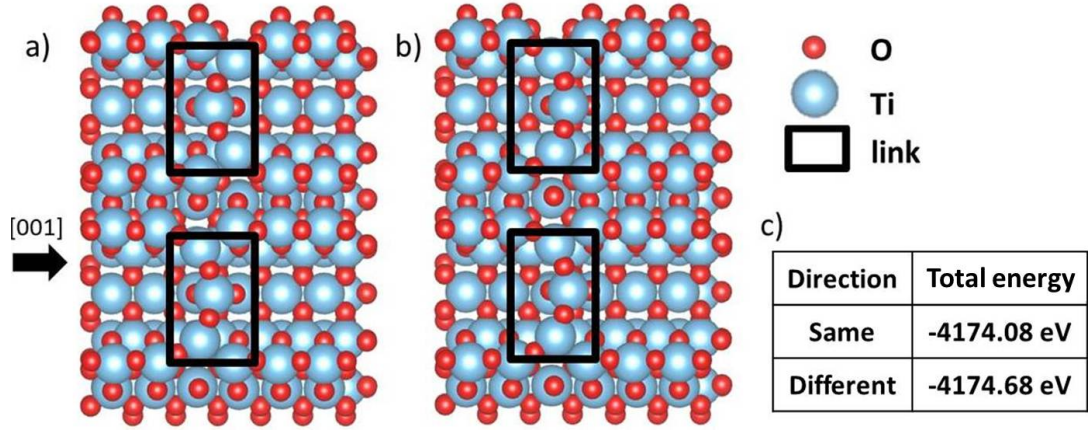


Figure 3.16: Space filling model after optimizing with a) different direction of neighboring single links, b) same direction of neighboring single links. c) is the energies of both structures. configuration constructed in a different direction exhibits a 0.6 eV lower total energy.

3.6 Discussion

This study reveals that, on the reconstructed rutile TiO₂(110)-(1 × 2) surface, the LDOS associated with oxygen and titanium atoms, as well as their bonding configurations, exhibit a pronounced inverse correlation with the actual atomic height in the vertical direction. This phenomenon is consistent with previous experimental and theoretical observations on the ideal TiO₂(110) surface[27]. On the (1 × 1) surface, the absence of bridging oxygen atoms leads to the partial reduction of neighboring five-coordinated titanium atoms (Ti^{5c}), resulting in the formation of localized defect states in the Ti 3*d* orbitals near the Fermi level, indicating electronic structure reconstruction induced by surface oxygen vacancies[28].

Similarly, localized electronic states are also observed on the (1 × 2) reconstructed surface, which is typically associated with the added-row structural model. Previous studies have shown that the formation of these states is strongly influenced by intrinsic or extrinsic defects, such as surface oxygen vacancies and subsurface titanium interstitials[29]. By correlating the LDOS features obtained from theoretical simulations with experimental scanning tunneling spectroscopy (STS) data, Ti³⁺ states associated with specific structural motifs can be effectively identified. This allows for a more precise distinction between natural and engineered surface defects. Such an approach not only deepens our understanding of the electronic properties of TiO₂ surfaces but also provides a microscopic perspective on the structure–property relationship critical for catalytic activity modulation.

Previous studies have demonstrated that the negative correlation between LDOS and atomic height could be attributed to the regulatory effects of the local bonding environment and electron density distribution[30]. Specifically, atoms at higher positions typically exhibit lower coordination numbers or weaker bonding interactions, which correspond to a reduced density of electronic states. Conversely, atoms located at lower positions tend to have higher LDOS due to stronger bonding or more concentrated local electron clouds. This phenomenon plays a pivotal role in stabilizing the Ti³⁺ state and facilitating the formation of defect states,

which may underpin the emergence of the link structure on the $\text{TiO}_2(110)-(1 \times 2)$ surface. Furthermore, the Ti^{3+} state is prone to localization in the form of small polarons, coupled with local lattice relaxation, an effect that further modulates carrier migration pathways and surface reaction activity[31, 32]. This observation also provides partial evidence suggesting that the link structure could confer a catalytic enhancement effect.

Moreover, these defect induced localized states have been confirmed to play a crucial role in photocatalytic processes, especially in charge trapping and transfer, which significantly affect the efficiency and selectivity of key reactions such as water splitting and CO_2 reduction[33, 34]. Further DFT studies demonstrate that the LDOS distribution in rich defect regions directly impacts the adsorption energies of catalytic intermediates, thereby altering reaction pathways and kinetics[35]. Based on this, LDOS features extracted from DFT simulations can serve as structural descriptors for machine learning models, enabling high-throughput predictions of surface reactivity on TiO_2 . This not only provides theoretical support for understanding and optimizing the photocatalytic performance of TiO_2 but also opens new avenues for catalyst screening.

3.7 Summary

In this study, we combined STM experiments with DFT simulations to utilized STM experiments and DFT simulations to conduct a systematic investigation of a single link structure within the $\text{TiO}_2(110)-(1 \times 2)$ surface reconstruction layer based on an asymmetric (1×2) structure. By comparing the STM images obtained from DFT simulations with those from the experiments, we verified the rationality of the single link structure based on asymmetric (1×2) model. Furthermore, by comparing the total energies of different link arrangements, we further evaluated the stability and rationality of the model. The results showed that the calculated optimal energy structure was highly consistent with the STM experimental images, further proving the validity and reliability of the model. This combined theoretical and experimental research method not only provided direct evidence for understanding the microscopic mechanism of $\text{TiO}_2(110)-(1 \times 2)$ surface reconstruction, but also laid a foundation for subsequent studies on surface defects, electronic localized states, and the detailed analysis of catalytic active sites.

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Chapter 4

Modeling and simulation of the double link on $\text{TiO}_2(110)-(1 \times 2)$ surface

4.1 Chapter description

This chapter systematically analyzed the structural characteristics of double link configurations on the $\text{TiO}_2(110)-(1 \times 2)$ surface by combining scanning tunneling microscopy (STM) experiments with density functional theory (DFT). From a structural perspective, we investigated the geometric arrangement, energetic stability, and possible interactions of the double links, providing a detailed understanding of their atomic-level configurations. Furthermore, by comparing simulated STM images based on DFT calculations with experimentally obtained STM images, the electronic structure features and local state distributions associated with the double link structures were further characterized, enabling a direct correlation between atomic geometry and experimentally observed contrast.

On this basis, this chapter also explored the relationship between double link and single link structures, and revealed a possible conversion mechanism between the two during surface reconstruction. The coexistence and interconversion of these structures suggest that the $\text{TiO}_2(110)-(1 \times 2)$ surface undergoes dynamic structural adjustment driven by energetic and kinetic factors. These results provide direct experimental evidence for the structural relationship between double and single links, and offer a reliable foundation for understanding the surface reconstruction mechanism and electronic structure characteristics of the $\text{TiO}_2(110)-(1 \times 2)$ surface. Meanwhile, the insights obtained from this systematic analysis provide important guidance and support for subsequent experiments and further investigations of surface structure evolution and functional properties.

4.2 Double link on the $\text{TiO}_2(110)-(1 \times 2)$ surface

TiO_2 is regarded as a prototypical functional metal oxide material due to its outstanding chemical stability, photocatalytic activity, and extensive applications in energy and environmental fields[1, 2, 3]. Among these, the (110) surface of rutile TiO_2 serves as a standard model system for studying oxide surface structures

and reactivity, owing to its highest thermodynamic stability and regular surface structure[4]. Under ideal conditions, the $\text{TiO}_2(110)$ surface exhibits a (1×1) periodic structure characterized by alternating rows of five-coordinate titanium (Ti_{3c}) atoms extending along the $[001]$ direction and bridging oxygen atoms[5, 6]. However, when subjected to high temperature vacuum annealing or exposure to reducing atmospheres, this surface spontaneously forms a reconstructed structure with (1×2) periodicity[7, 8]. Numerous studies have demonstrated the potential of this surface in terms of surface activity[9, 10, 11, 12, 13]. The formation mechanism of this structure and the arrangement of its atoms have long been an important topic in surface science research. This provides crucial reference for further studies on the adsorption behavior of water molecules and its impact on surface chemical reactions[14, 15].

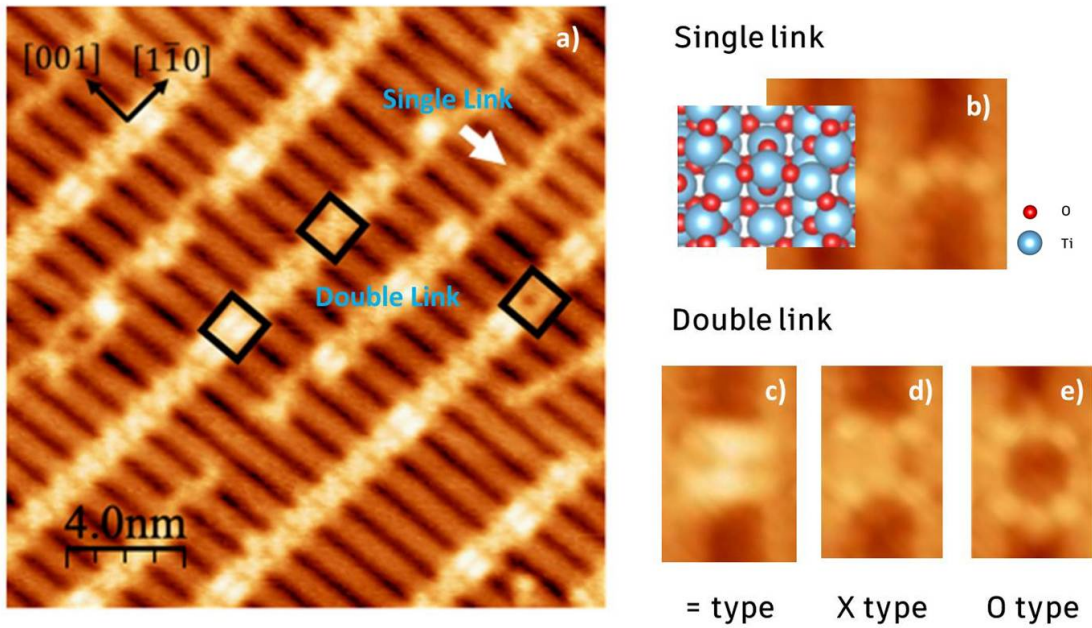


Figure 4.1: STM image with all type links and different types of double link structure on the $\text{TiO}_2(110)-(1 \times 2)$ surface. a) is STM image of the clean $\text{TiO}_2(110)-(1 \times 2)$ surface with all types link structure, the sample bias voltage was 1.5 V. b) is the single link modeling with STM images. c), d), e) are the STM image of = type, X type O type, respectively.

By analyzing the STM images, it can be observed that the dark stripes along the $[001]$ direction form a (1×2) region, and the bright stripes along the $[1\bar{1}0]$ direction correspond to the link structure. Among the link structure, the shorter stripes extending along the $[001]$ direction represent the single link structure, and the extracted structure is shown in the figure. The longer stripes extending along the $[001]$ direction represent the double link structure. Based on the differences in the local brightness distribution and characteristic patterns presented in the STM images, double link can be further divided into three types: X type, = type, and O type. The images are shown in Fig.4.1.

In previous research, the asymmetric structure of the (1×2) region has been experimentally validated through multiple approaches[9, 8, 16]. Since many studies on the $\text{TiO}_2(110)-(1 \times 2)$ surface are based on the symmetrical (1×2) region[17,

18, 19], this conclusion necessitates a re-evaluation of the precise conformational characteristics of the linking region. For the single link structure, building upon the symmetric (1×2) framework, a widely recognized model has been put forward[18, 17], with subsequent investigations refining and corroborating it based on the asymmetric (1×2) configuration. In contrast, current research on the double link structure remains insufficient to fully elucidate its structural arrangement and compositional details. Historically, the double link structure was frequently conceptualized as an assembly of single link motifs[18, 17], a conclusion seemingly supported by structural hypotheses proposed in numerous studies, however, this proposition lacks empirical experimental substantiation. Notably, the double link structure exhibits a substantially higher surface abundance compared to its single link counterpart. Gaining insight into this structure is therefore pivotal for identifying potential surface active sites and deciphering surface catalytic mechanisms. Additionally, studies have demonstrated that water molecules can form interactions with the double link structure under specific conditions[20]. Thus, structural analysis of the double link architecture will facilitate a deeper understanding of the surface’s intrinsic properties.

Most previous research on double links has focused on one specific type, the X type[17, 19, 21]. However, as research in this area has progressed, an increasing number of different types of double links have been discovered, including the = type and O type. There is still a significant gap in potential structural models. It is worth noting that the current understanding of the X type is based on the assumption of a symmetrical (1×2) structure. However, this assumption has been challenged by multiple recent experimental results, suggesting that models based on this assumption may be inaccurate. Furthermore, some subsequent simulation studies have not clearly depicted conformational changes in the (1×2) region, and the evidence supporting the rationality of the existing model is insufficient. This situation has increased the difficulty of conducting further analysis on the surface.

In this study, we aim to comprehensively analyze the structure of all double links based on the asymmetric (1×2) region. Through STM simulation technology, we provide experimental support for the conclusion. And based on the structure, we propose the relationship between double links and single links.

4.3 Experiment

STM measurements were performed using a self-built STM system under ultra-high vacuum (UHV) conditions (base pressure below 1.0×10^{-10} Torr) at room temperature, following the same experimental procedures described previously. Nb-doped (0.05 wt%) rutile $\text{TiO}_2(110)$ single-crystal substrates were used. The $\text{TiO}_2(110)$ -(1×2) reconstructed surface was prepared by repeated cycles of Ar^+ ion sputtering and annealing under identical conditions.

DFT calculations and STM image simulations were performed to investigate the atomic and electronic structures of the $\text{TiO}_2(110)$ -(1×2) surface. All calculations were carried out using the Vienna Ab initio Simulation Package (VASP)[22, 23] with the projector augmented wave (PAW) method[23, 24]. Exchange–correlation effects were treated within the generalized gradient approximation using the Perdew–

-Burke-Ernzerhof (PBE) functional[25]. Partial valence (pv) potentials were employed to include Ti $3s$ and $3p$ semicore states.

Geometry optimizations were performed until the residual forces on all atoms were below $0.025 \text{ eV/\AA}$. The optimized structures were then used for STM image simulations. Simulated STM images were generated using the p4vasp package (version 0.3.29) within the Tersoff–Hamann approximation, in constant-current mode at a sample bias of $+1.5 \text{ V}$, corresponding to unoccupied-state imaging. The simulated images were compared with experimental STM data to elucidate the (1×2) surface reconstruction and the influence of Nb doping on the surface electronic structure.

4.4 Result

Initial model

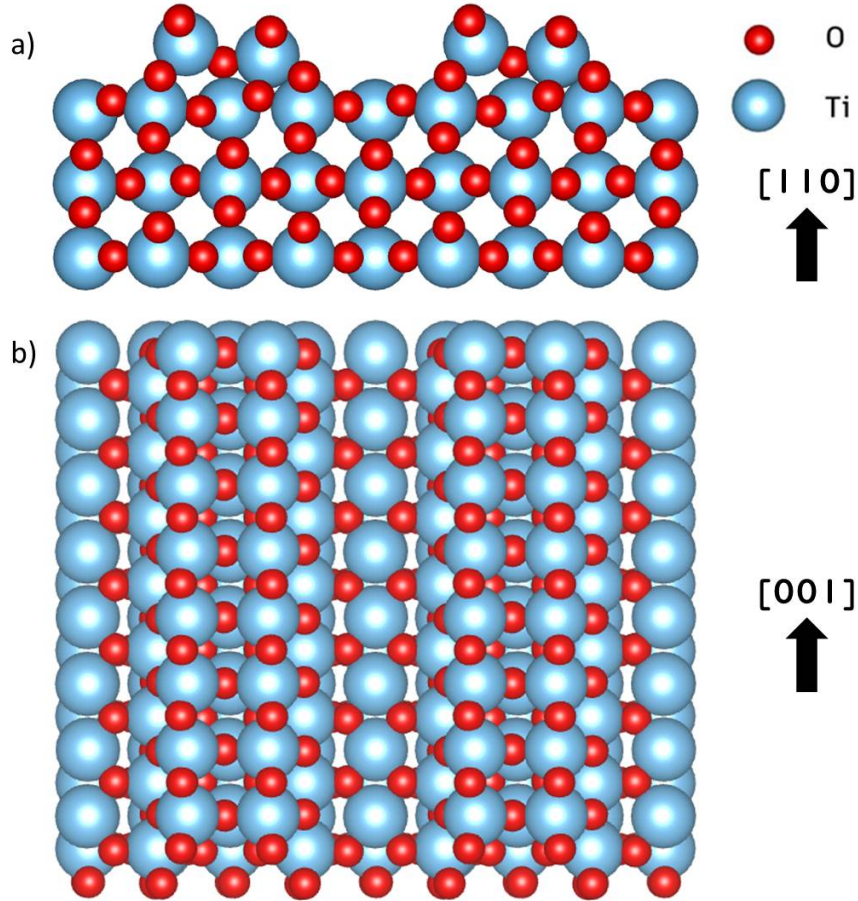


Figure 4.2: The space filling model of the initial (1×2) region without link region, the bottom two atomic layers are fixed. a) Side view of the model, b) Top view of the model.

In chapter3, we introduced the modeling that does not include link region. We expanded the basic structure so that the link can ensure symmetry along $[001]$ and the spacing between the link column is at least no less than the shortest

distance visible in the STM image. However, in the optimization of double link, we do not need to ensure symmetry. At the same time, the distance along the $[001]$ direction needs to be further increased because double link is "thicker" than single link. Therefore, the distance required to maintain the minimum spacing is also longer.

The final model was constructed as a $2 \times 8 \times 1$ supercell. Compared with the previous model, we have extended along the $[001]$ direction, adding two sets of (1×2) structures in this direction. This ensures that the spacing between the double links is greater than 2 nm. At the same time, we have not reduced the bidirectional structure in the a direction. This is because the adjacent double links is expected to be of different types. For example, in the STM images, no adjacent O type was observed. Therefore, in the simulation of this type, we will make them adjacent to other types to ensure accuracy. The parameters used in the calculation are all the same as those obtained in the previous chapter. The final model is shown in Fig.4.2.

= type

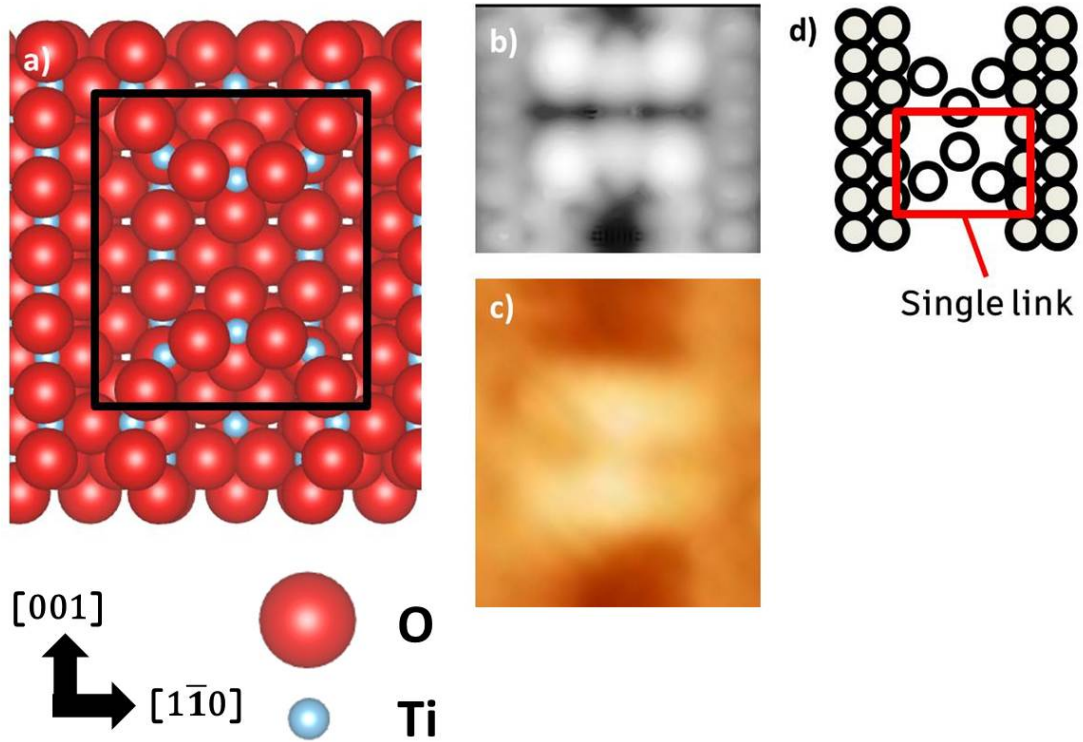


Figure 4.3: a) Space-filling model of = type , b) the STM simulation image of the model in a), c) the actual STM image of = type , d) the schematic diagram of the relationship between the = type and single link

Fig.4.3-a) illustrates the optimized type-structured model. As revealed by the STM simulation image(Fig.4.3-b)), the simulated topography of this model exhibits a high degree of consistency with the experimental STM results(Fig.4.3-c)). Both the two equal length, bright regions and the connecting structure between

them are accurately reproduced. This congruence suggests that the model well captures the geometric configuration and electronic structure of the experimental system. From a structural evolution perspective, this connecting structure forms when two opposing single links gradually approach each other under mutual attraction. Upon reaching a "contact" state, the originally dispersed link structures transform into a more linear configuration. In this state, the originally dispersed and randomly arranged link structures within individual single links gradually transform into a more linear configuration as the interchain distance decreases and the interaction strengthens. This structural transition is likely associated with the mutual influence between Ti atoms in the two single links: upon approaching, the local electron density undergoes redistribution, stabilizing the more linear configuration and yielding STM brightness characteristics that are highly consistent with experimental observations.

X type

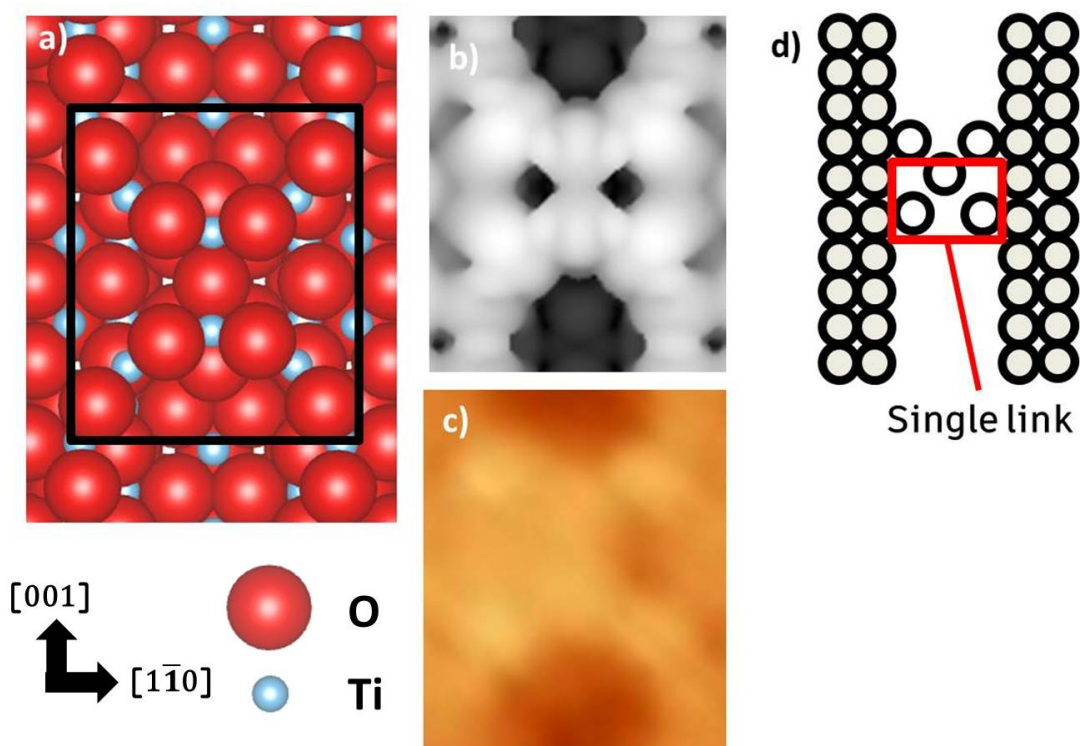


Figure 4.4: a) Space-filling model of X type , b) the STM simulation image of the model in a), c) the actual STM image of X type , d) the schematic diagram of the relationship between the X type and single link.

Fig.4.4-a) depicts the optimized X type structural model. The simulated STM images(Fig.4.4-b)) exhibit general consistency with the experimental images(Fig.4.4-c)), both clearly resolve the characteristic X-shaped architecture, and within the vicinity of the (1×2) unit cell region, shadow-like features are observed that align well with those in the experimental images. Considering the inherent resolution discrepancy between experimental and simulated STM images, as well as the approximate nature of the simulation methodology employed, the simulated

results are deemed to possess high credibility. Although the (1×2) column itself has obvious asymmetry, the X type link structure is still able to maintain a relatively good overall symmetry. Its final optimized configuration is basically consistent with the link structure proposed previously based on the symmetric (1×2) model. We observed that varying the initial position of second-layer atoms in X type links sometimes causes lateral displacement during optimization, resulting in significant geometric distortion. As a result, the brightness distribution and structural features of the simulated STM images will deviate significantly from the actual experimental images. Therefore, it can be concluded that maintaining the reasonable position of the atoms in this layer is crucial for reproducing STM images that conform to the experimental characteristics, and also ensures the reliability and physical rationality of the model structure. From the perspective of structural formation mechanism, the X type structure resembles the = type in that both are formed by two individual linkages gradually approaching each other from opposing directions. However, in contrast to the = type, the two constituent linkages in the X type structure are spaced more closely, with local atoms exhibiting a tendency toward spatial overlap or sharing specifically, both occupy positions that would otherwise be associated with the same oxygen atom. This more compact bonding mode confers greater energetic stability to the X type structure, which is consistent with the statistical distribution of different structural configurations observed in STM imaging.

O type

Fig.4.5-a) presents the optimized O type structure model. In this model, the orientation of the single link is opposite to that of the two previously constructed models. Based on the observed feature of the double link size similar to that in the STM images, the model selects the configuration of single atomic spacing, causing the "missing sides" of the two single links to be arranged relative to each other, thereby forming an empty space in the middle. This empty space is manifested as a clear void in the simulated STM image, which is highly consistent with the local bright and dark features observed experimentally. This result demonstrates the rationality of the model. Based on this, we also optimized the parameters of the model where the distance between single links was further increased. However, we found that the model was prone to discrete phenomena under this condition. In the surface structure, the proportion of the O type structure is the smallest. In the large area STM images, we rarely observed continuous O type arrangements, which further indicates the relative instability of this structure. Although there are slight differences in certain details between the simulated STM images and the experimental images, when considering the proportion, spatial distribution, and local features, such differences are acceptable and do not affect the reasonable explanation of the formation mechanism and local features of the O type structure.

The relationship between links

Fig.4.6 illustrates the relationship between single links and double links derived from our simulation results. When two single links with different orientations approach each other, they can combine to form three distinct types of double links.

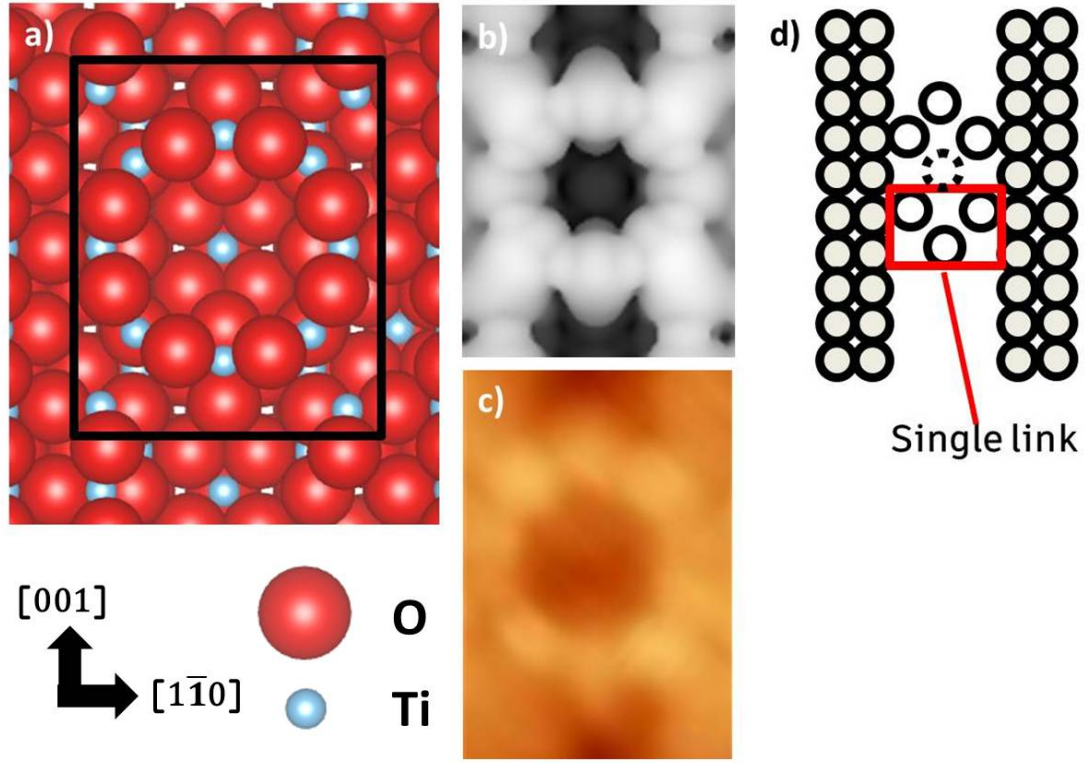


Figure 4.5: a) Space-filling model of O type , b) the STM simulation image of the model in a), c) the actual STM image of O type , d) the schematic diagram of the relationship between the O type and single link.

Specifically, as the two protruding atoms gradually move closer to adjacent positions, = type double link is formed. This configuration represents an intermediate stage where the atoms are in close proximity but do not yet share the same site. As the atoms approach further, they eventually occupy the same lattice site and share an oxygen atom, resulting in the X type double link, which exhibits the largest surface coverage among the three types. This process indicates that the X type double link represents the energetically most favorable configuration under high local density conditions. In contrast, when two single links with opposite directions approach each other, a different interaction pattern emerges. Due to their opposite orientations, a vacancy remains between the two protruding atoms, leading to the formation of an O type double link.

Overall, this structural evolution emphasizes the decisive role of the relative arrangement of single atoms in determining the type of double link formed. The simulations suggest that the spatial distribution, local surface coverage, and stability of double links are strongly influenced by several key factors: the orientation of the single links, the relative positions of protruding atoms, and the presence of vacancies or unoccupied sites. These findings provide a comprehensive understanding of how single link arrangements dictate the formation and local characteristics of double links, offering valuable insights into surface reconstruction processes and the factors controlling surface structure evolution.

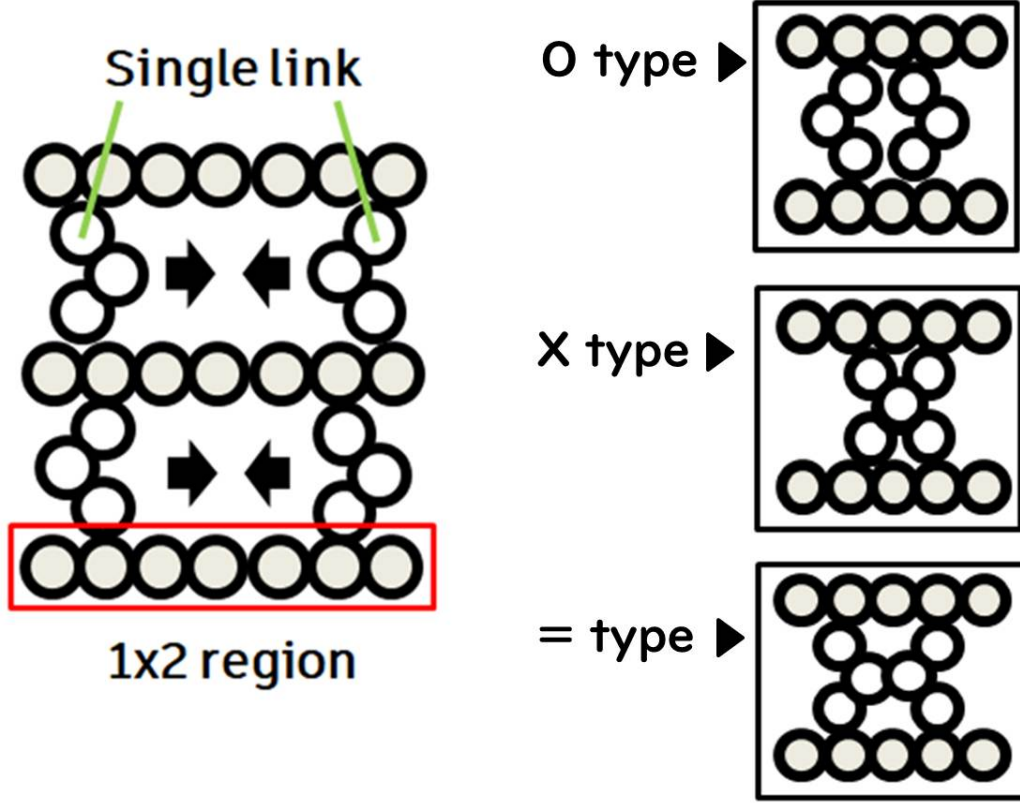


Figure 4.6: Relationship between the single link structure and the double link structure. On the left is a schematic diagram showing the gradual convergence of the single link structure, and on the right is the formed double link structure.

4.5 Discussion

From our experimental process, as the number of annealing cycles increases, different types of link structures will gradually appear on the $\text{TiO}_2(110)-(1 \times 2)$ surface, and the proportion of each type of link structure will change with the increase in the number of annealing cycles. Although we have demonstrated the formation relationship between single link and double link, in the actual process, it is not a strict sequential formation pattern of single link first and then combination. From the structure perspective, neither the O type nor the = type has broken away from the structure of single link; they are just different forms due to a relatively close distance. The X type structure is more closely connected, and there is interaction between single links. It is also the type with the largest surface proportion.

Previous studies have shown that the $\text{TiO}_2(110)-(1 \times 2)$ double link surface exhibits significantly different electronic structure characteristics at the local scale. Through scanning tunneling spectroscopy (STS), it was found that this surface has multiple band gap states, whose energy positions and intensities are closely related to the specific connection structure[26]. This indicates that the double link structure not only determines the atomic geometric arrangement but also directly regulates the local state density and the spatial distribution of Ti^{3+} related electronic states. Two distinct energy gaps exist, one at 0.7 eV, another at 1.5 eV, and an additional energy level at 1.1 eV. These energy levels may correspond to the

relatively high proportion of single link and X type structures, while the additional energy level may represent the relatively lower proportion of = type structures[26]. More importantly, these band gap states related to the double link structure have been proven to be active in the surface adsorption and reaction processes[27, 28, 29]. For example, the adsorption of oxygen molecules significantly weakens these band gap states and causes an increase in the surface work function, indicating that electrons transfer from the $\text{TiO}_2(110)-(1 \times 2)$ surface to the adsorbate[30, 31, 32]. Therefore, the change in the proportion of the connection structure during the annealing process not only means structural evolution but may also directly affect the adsorption ability, catalytic activity, and electron transfer behavior of the $\text{TiO}_2(110)-(1 \times 2)$ surface.

Based on the above understanding, the evolution of the proportion of connection structures during the annealing process can be further regarded as an effective means to regulate the electronic structure and functional properties of the $\text{TiO}_2(110)-(1 \times 2)$ surface. This study shows that as the number of annealing cycles increases, the relative proportions of different types of connection structures undergo systematic changes, which implies that the band gap state density and its spatial distribution related to them may also be adjusted accordingly. Since these band gaps play a crucial role in electron transfer, molecular adsorption, and surface reactions, controlling the annealing process to regulate the proportion of connection structures is expected to achieve indirect regulation of surface adsorption ability, catalytic activity, and reaction selectivity.

4.6 Summary

This research systematically constructed and analyzed models of different types of double link structures on the $\text{TiO}_2(110)-(1 \times 2)$ surface. Based on the single link model, we established the initial double link model by expanding the single link spacing and considering the shortest distance visible in the STM images. We then further optimized to obtain three typical double link structures: = type, X type and O type. The simulated STM images were highly consistent with the experimental results, verifying the rationality and accuracy of the model.

Specifically, the single links approach each other in the opposite directions, highlighting the relative positions of the atoms. This leads to the formation of the = type. Then, the two single links continue to approach each other until the protruding atoms overlap. This results in the X type. When the protruding atoms are facing each other in opposite directions, they approach each other until there is a distance of an oxygen vacancy between them, forming the O type.

Overall, the formation mechanism of the double-stranded structure is mainly influenced by the relative orientation of the single strands, the local atomic positions, and the presence of vacancies. Different arrangements directly determine the type of double link structure, the surface coverage, and the distribution of local electronic structures, thereby affecting the STM characterization features. This study not only reveals the double link structure on the $\text{TiO}_2(110)-(1 \times 2)$ surface, but also reveals the atomic-scale formation rules of the double link structure and the single link structure.

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Chapter 5

Water adsorption on $\text{TiO}_2(110)-(1 \times 2)$ surface

5.1 Chapter description

TiO_2 is widely used as a catalytic material[1]. Investigating its surface characteristics at the nanoscale can help elucidate the underlying catalytic mechanisms and potentially enhance its efficiency[2, 3]. One key surface of interest is the $\text{TiO}_2(110)-(1 \times 2)$ reconstructed surface, which forms under oxygen reduction and high-temperature annealing in UHV conditions.

Previous studies have proposed an asymmetric Ti_2O_3 model for this reconstruction[4, 5, 6], where specific link structures on the surface may contribute positively to catalytic reactions. A critical direction in TiO_2 catalysis research involves water decomposition, and studying water adsorption on the surface can provide insights into the reaction mechanisms and principles[7, 8].

Earlier work has reported that water can adsorb on the $\text{TiO}_2(110)-(1 \times 2)$ surface at room temperature, and theoretical studies have also supported a molecular adsorption mode[9, 10]. However, the detailed mechanism of water adsorption and its impact on the reconstructed surface remain unclear.

In our study, we perform long-term water adsorption imaging using STM and LEED measurements to investigate the dynamics of the adsorption process. Our findings show that the surface structure and link features evolve with annealing at different temperatures post water adsorption, indicating that water plays a significant role in modifying the link structure and potentially affecting the surface's catalytic process. In this chapter, the emergence of a previously unreported double-cross-link structure induced by water adsorption followed by moderate thermal annealing, and demonstrate its reversible nature is discussed.

5.2 Study of water adsorption

The rutile $\text{TiO}_2(110)$ surface is the most stable facet of rutile TiO_2 and has therefore been extensively investigated[11, 12]. In particular, the $\text{TiO}_2(110)-(1 \times 1)$ surface is widely studied due to the relative ease of preparing well-defined, clean surfaces[13, 14, 15]. Oxygen vacancies on this surface are known to enhance water adsorption, with numerous studies demonstrating that water dissociates preferen-

tially at these defect sites, a process relevant to photocatalytic activity[16, 17, 18]. Water adsorption on TiO_2 surfaces plays a pivotal role in photocatalytic reactions, as it is directly involved in the formation of surface hydroxyl species and serves as a primary reactant in oxidation and reduction processes[6, 19, 20]. The adsorption configuration and dissociation behavior of water critically influence charge transfer, reaction pathways, and overall catalytic efficiency[12, 21].

High-temperature annealing of $\text{TiO}_2(110)-(1 \times 1)$ under ultrahigh vacuum conditions leads to the formation of the $\text{TiO}_2(110)-(1 \times 2)$ reconstructed surface, which has attracted increasing attention due to its enhanced surface reactivity[22, 23]. Scanning probe microscopy studies have revealed complex and asymmetric structural features on $\text{TiO}_2(110)$ surfaces, suggesting an increased density of oxygen deficient sites[2].

Previous studies indicate that the $\text{TiO}_2(110)-(1 \times 2)$ surface may exhibit higher catalytic activity than the (1×1) surface, as demonstrated in reactions such as the decomposition of trimethyl acetic acid and enhanced photoresponse under ultraviolet irradiation [24]. Although water adsorption on $\text{TiO}_2(110)-(1 \times 2)$ has been observed at room temperature[21], the adsorption mechanisms, preferred sites, and stability of adsorbed water remain poorly understood[17, 25]. Furthermore, the role of specific surface structural units in mediating water adsorption and catalytic activity requires further investigation.

5.3 Experiment

All experiments were carried out using a home-built STM operated at room temperature under ultrahigh vacuum conditions ($< 10^{-8}$ Pa). Both platinum and tungsten STM tips were used. $\text{TiO}_2(110)$ substrates doped with niobium (0.05wt%) were used. Prior to introduction into the UHV environment, the samples were cleaned by sequential ultrasonic treatment in acetone and ultrapure water. After degassed at 500°C for 12 hours at $\sim 10^{-8}$ Pa, the samples were Ar^+ -sputtered ($\sim 10^{-4}$ Pa, 1.2 keV, 15 min) and annealed repeatedly. Annealing was performed at 800°C until the (1×1) surface structure was obtained, then the temperature was increased to 900°C to obtain the (1×2) . Surface structures were checked by low energy electron diffraction (LEED) and STM. For water adsorption, ultra pure water was placed in a single tube for ultrahigh vacuum and a variable leak valve was used to adjust the exposure. To further purify the water in the single tube, the ultra pure water was frozen with liquid nitrogen from outside, and the variable leak valve was opened fully to pump impurities several times.

5.4 Water adsorption

Experimental process

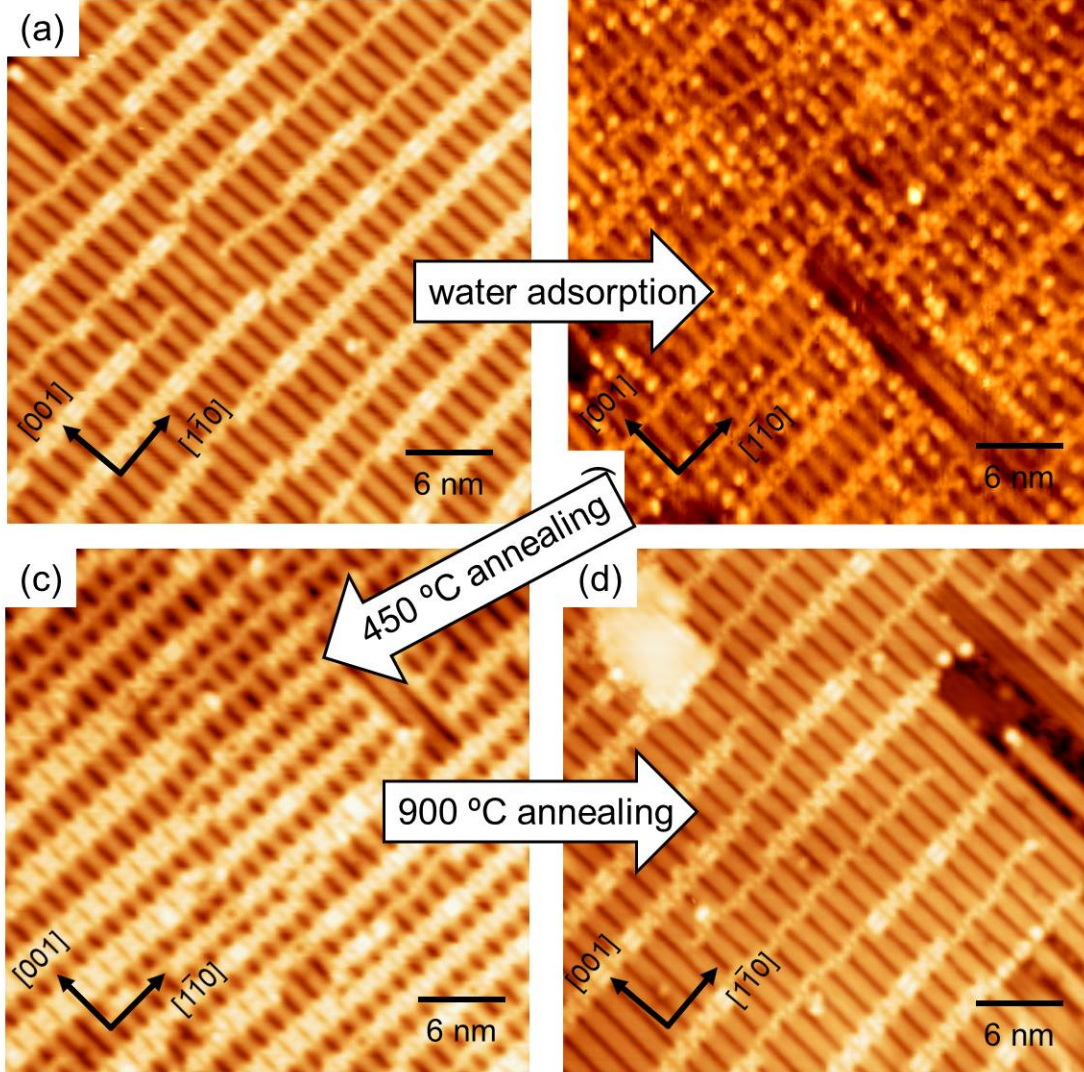


Figure 5.1: STM images of the rutile $\text{TiO}_2(110)-(1 \times 2)$ surface. a) Clean surface, b) water-adsorbed surface (100.8 Langmuir), c) water-adsorbed surface annealed at 450 °C, d) surface from c) further annealed at 900 °C. The tunneling current setpoint was 100 pA for a) 1– d), respectively. The sample bias voltage was 2.0 V for a), b), and d) and 2.5 V for c), respectively.

On the $\text{TiO}_2(110)-(1 \times 2)$ surface, we investigated water adsorption and subsequent surface modifications. Specifically, we examined surface changes following water adsorption at an exposure of 100.8 Langmuir, and after sequential annealing at 450 °C and 900 °C. Fig.5.1 presents STM images of (a) the clean surface, (b) the surface after water adsorption, (c) the surface annealed at 450 °C post-adsorption, and (d) the surface further annealed at 900 °C. After water exposure, numerous bright spots appear in the STM images (Figure 5.1-b), which were not present

on the pristine surface. Continuous STM imaging during water introduction into the chamber revealed a gradual increase in the number of these bright spots over time. This observation suggests that the bright features correspond to adsorbed water-related species, such as intact H_2O molecules or dissociation products. Importantly, despite the appearance of these new features, the underlying (1×2) reconstructed surface—including its periodic structure and link motifs—remains largely intact. This preservation of surface morphology upon water adsorption aligns well with previous reports in the literature.

Although the exact nature of these bright spots is not yet fully clear, their existence clearly indicates that water molecules can adsorb on the $\text{TiO}_2(110)-(1 \times 2)$ surface. Despite the presence of the adsorbates, the (1×2) reconstructed structure of the TiO_2 surface is still maintained, suggesting that the water adsorption did not significantly disturb the overall surface lattice or trigger large scale atomic rearrangement. To further investigate the interactions between these adsorbates and the surface and their thermal stability, we conducted annealing experiments at 450 °C and 900 °C. The choice of these high temperature conditions was to promote possible surface reactions or structural evolution, so as to observe the behavioral changes of water-related species on the $\text{TiO}_2(110)-(1 \times 2)$ surface. For example, annealing at 450 °C can provide sufficient thermal activation energy to cause the local evaporation of adsorbed water molecules without destroying the overall reconstruction, while the high-temperature annealing at 900 °C is the temperature at which the surface can enter a more stable structure. Through these annealing experiments, the kinetic stability of water adsorption species, the strength of their interaction with the surface structure, and temperature-dependent behavior can be systematically analyzed. These pieces of information can help understand the stability of the $\text{TiO}_2(110)-(1 \times 2)$ surface in a humid environment, and also provide important references for revealing the microscopic mechanisms of its catalytic reactions, surface chemical activity, and water-related surface reactions.

Remarkably, annealing the water-adsorbed surface at 450 °C resulted in the formation of a unique, wide-bridging structure clearly distinguishable from the single link and double link structures observed on the clean and water-adsorbed surfaces (Fig.5.1-c)). This striking transformation suggests that the interaction between the adsorbed water-related species and the $\text{TiO}_2(110)-(1 \times 2)$ surface at elevated temperatures induces significant structural changes, potentially leading to the creation of novel surface features with distinct properties and reactivity. Upon annealing at 900 °C following the initial 450 °C heat treatment, a distinct structural transformation occurs. The majority of the surface undergoes a significant reconstruction, reverting to the original (1×2) surface structure. This recovery suggests that the high-temperature annealing provides sufficient energy to overcome the structural changes induced by water adsorption and the subsequent 450 °C annealing. However, intriguingly, some regions of the surface resist this transformation, retaining a (1×1) structure or remaining disordered. These persistent structural variations hint at the complexity of the interactions between the adsorbed species and the $\text{TiO}_2(110)$ surface, as well as the potential for locally stabilized surface configurations. The presence of multiple structural configurations on the surface after annealing at 900 °C suggests complex mechanisms governing the surface reconstruction and the stability of water-induced structural changes. The formation of a distinctive link structure on the water-adsorbed sur-

face after annealing at 450 °C (Fig.5.1-c)) prompted a detailed investigation using high-resolution STM imaging and line profile analysis.

5.4.1 Clean $\text{TiO}_2(110)$ -(1 × 2) surface

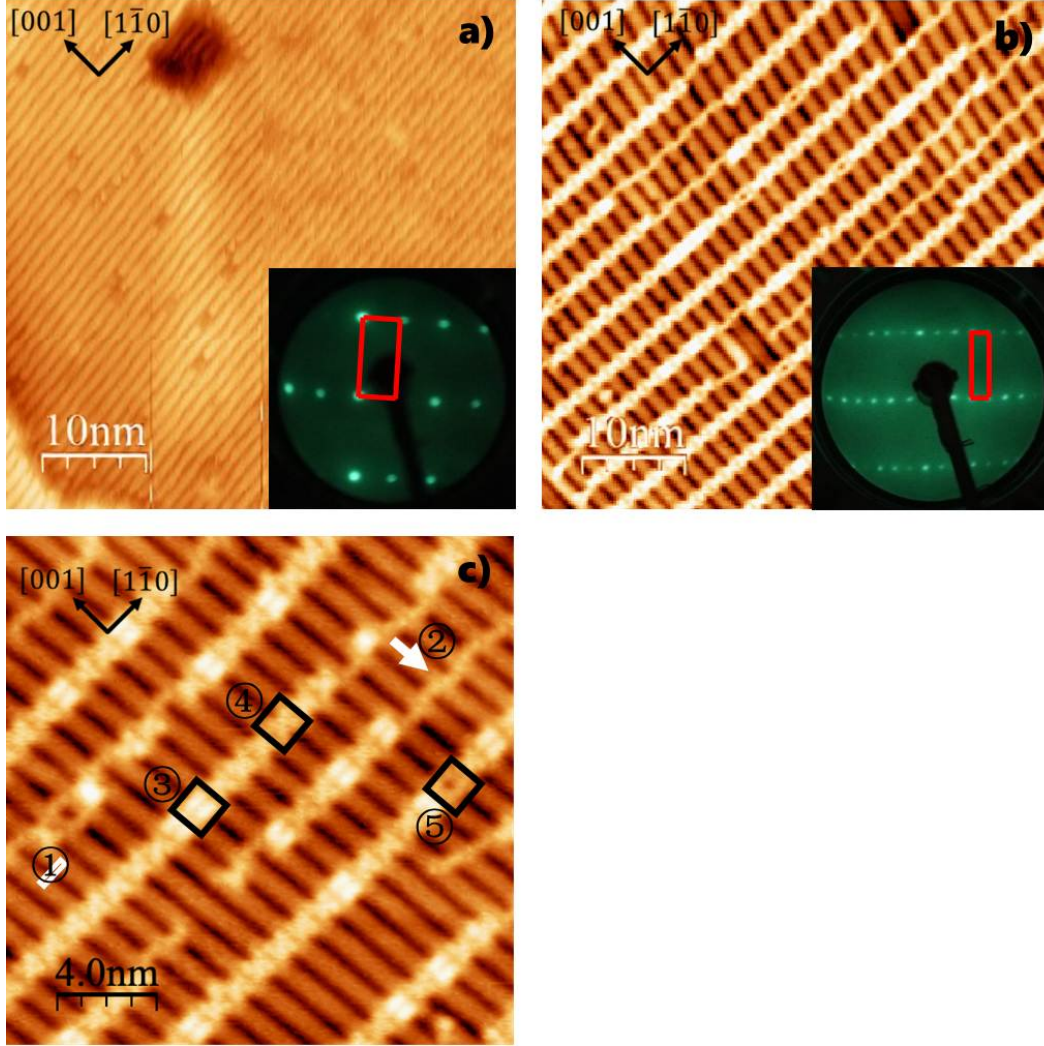


Figure 5.2: STM image and LEED pattern of the rutile $\text{TiO}_2(110)$, acquired with a tunneling current setpoint $I_t = 100$ pA and a sample bias voltage $V_s = 2.0$ V. a) is the (1 × 1) surface and b) is the (1 × 2) surface. c) is the different parts of the $\text{TiO}_2(110)$ -(1 × 2) surface, ① is the (1 × 2) region, ② is the single link, ③, ④, ⑤ are all double links, which are = type, X type, and O type, respectively.

Since the $\text{TiO}_2(110)$ -(1 × 2) surface cannot be gotten directly, it was obtained in this experiment by subjecting a $\text{TiO}_2(110)$ -(1 × 1) surface to repeated cycles of sputtering and high-temperature annealing. A TiO_2 sample doped with 0.05 wt% Nb was used as the substrate. Fig.5.2 illustrates the transformation process from the initial (1 × 1) surface to the (1 × 2) reconstructed surface. Through multiple sputtering and annealing cycles, the surface gradually evolved from the unreconstructed (1 × 1) structure to a well defined (1 × 2) reconstruction. This

transformation was driven by surface energy minimization under high-temperature conditions, with the annealing temperature maintained at approximately 900°C. Both LEED and STM images confirm the successful and complete reconstruction of the surface. The resulting (1×2) structure exhibits clear linear features characteristic of the reconstruction. Additionally, random-area STM scans further verify that a majority of the surface has been uniformly and cleanly reconstructed into the (1×2) phase, indicating a high degree of surface homogeneity.

Fig.5.2-c) presents an STM image of the rutile $\text{TiO}_2(110)$ - (1×2) surface alongside a structural model of the (1×2) reconstruction. The surface exhibits an asymmetric, periodically repeating row structure, with a periodicity that is twice that of the underlying bulk lattice along the $[001]$ direction. The STM image reveals several notable surface features characteristic of the (1×2) reconstruction. Among these are line defects, where sections of the periodic rows appear darker, indicating local disruptions in the row structure. In addition, distinct bridging structures are observed, including both single link and double link features. The double link structures can be further categorized into cross link(X type link), equal-shape link(= type link), and O-shape link(O type link) configurations, each representing different bonding geometries between adjacent rows.

5.4.2 Continuous water adsorption

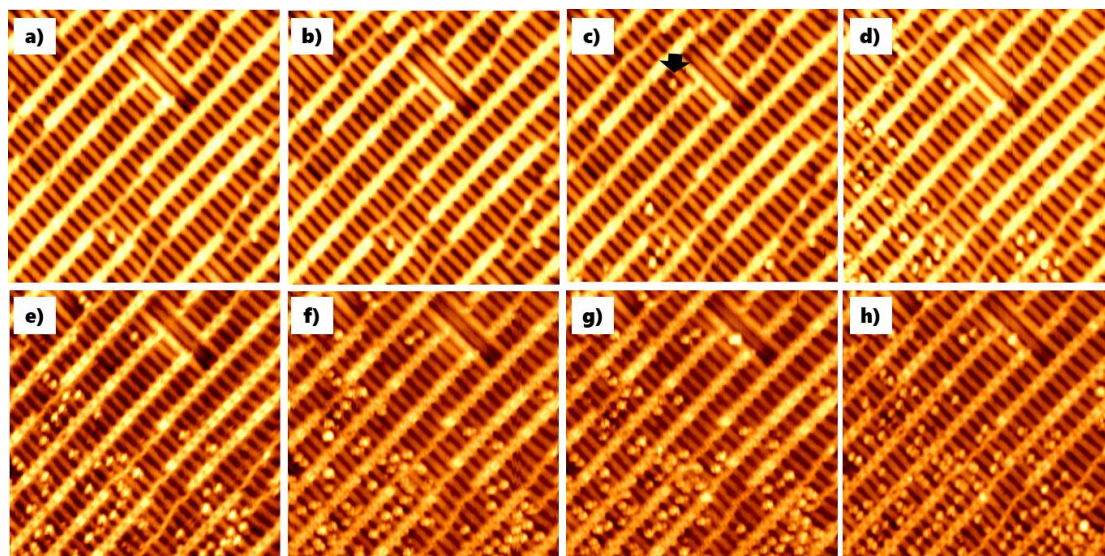


Figure 5.3: STM images of continuous water adsorption on the rutile $\text{TiO}_2(110)$ - (1×2) surface. a) before water adsorption(0 Langmuir), b) after drift compensation(0 Langmuir), c) 16 Langmuir, d) 31 Langmuir, e) 47 Langmuir, f) 62 Langmuir, g) 94 Langmuir, h) 110 Langmuir. Tunneling current setpoint and sample bias voltage were 100 pA and 2.5 V, respectively.

Fig.5.3 presents the time-resolved STM sequence of the $\text{TiO}_2(110)$ - (1×2) surface under constant water vapor exposure conditions, clearly capturing the dynamic evolution process of water molecule adsorption. This sequence not only reveals the site selectivity of molecular adsorption but also provides atomic-scale intuitive evidence for the evolution law of coverage over time, which is helpful for under-

standing the adsorption kinetics and the influence of local surface structure on the adsorption behavior.

As shown in Figure 5.3-a), before the water dosage was applied, the original surface maintained a highly ordered 1×2 reconstruction pattern, and the surface structure could be clearly distinguished. To ensure the precise alignment of consecutive images in space, this study employed a self-made image processing program. This program can perform nonlinear drift correction and stabilize the scanning area, making it possible to reliably compare the same atomic-scale regions at different time points, thereby achieving precise tracking of adsorption dynamics[26, 27]. Fig.5.3-b), acquired ten minutes later, confirms that the scanning area remained unchanged after correction, establishing a robust baseline for tracking adsorption events.

Upon initiating water exposure at a controlled, constant dosing rate, discrete bright spots began to emerge on the (1×2) reconstructed surface. These spots are attributed to individual water molecules or water-derived species adsorbing at specific sites, likely atop undercoordinated Ti atoms that act as favorable adsorption centers. The appearance of these features is consistent with previous STM studies of water.

As the exposure progressed, the density of white spots increased steadily, demonstrating a coverage-dependent adsorption process. Interestingly, all newly formed spots were confined exclusively to the (1×2) regions, and no such features were observed on or within the line defect zones. This spatial selectivity was confirmed by repeated experiments under identical conditions, indicating that line defects either lack suitable adsorption sites or are passivated under UHV annealing conditions. The absence of adsorption activity in these regions suggests a localized difference in electronic structure or steric hindrance that prevents water uptake. Eventually, the growth in spot density slowed, and a saturation point was reached, beyond which no further adsorption events were observed. This plateau behavior indicates that the available active sites on the (1×2) domains became fully occupied. In order to further observe information such as the adsorption rate and saturation degree, we conducted further statistics on the number of surface bright spots and the amount of water exposure.

coverage

Fig.5.4 illustrates the trend of the number of atoms in different surface areas changing with the increase in water exposure in two sets of experiments. STM images reveal that both curves show a significant rapid increase in the low exposure range, indicating that in the initial stage of adsorption, there are a large number of available adsorption sites on the surface, and water molecules can efficiently occupy these sites, resulting in a high reaction efficiency of the adsorption process. As the amount of water exposure continues to increase, the growth rates of the two curves gradually slow down and eventually become saturate. Their overall shape is highly consistent with the typical Langmuir adsorption curve. This behavior indicates that as the adsorption process progresses, the available adsorption sites on the surface are gradually occupied. Once most of the sites are filled, the newly added water molecules find it difficult to continue adsorbing, and the system eventually reaches the adsorption saturation state. Although there are certain differences in

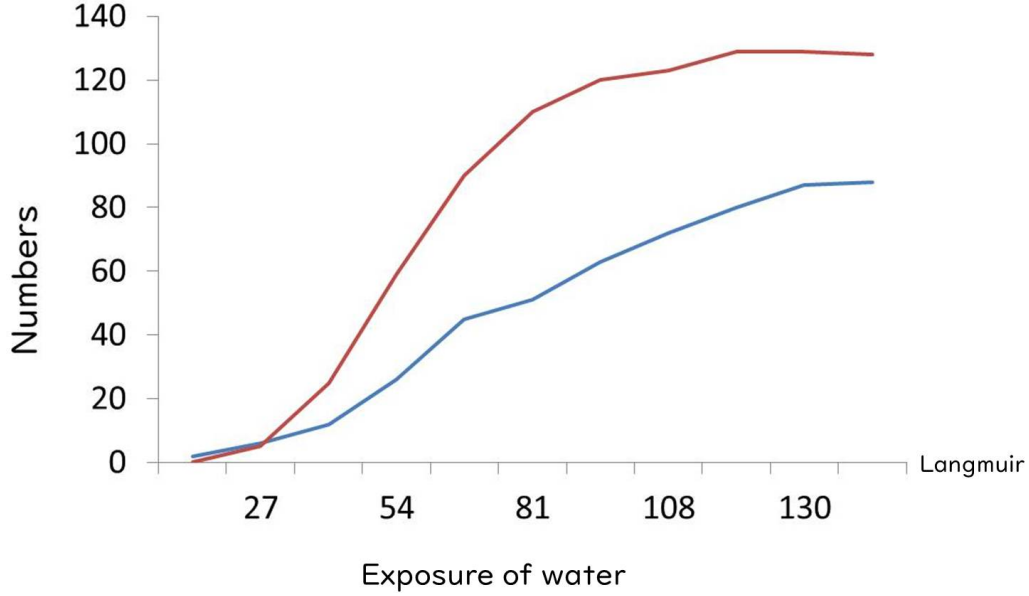


Figure 5.4: Line graph showing the change in the number of atoms in different regions as the amount of water adsorption becomes exposed. The x-axis represents the exposure amount (Langmuir), and the y-axis represents the number of atoms in the corresponding region. The two curves in the graph represent the atomic accumulation situation of the surface region during the exposure process in two different experiments.

the number of atoms corresponding to different surface regions when they reach saturation, this might be due to the differences in local surface structure, atomic coordination environment, or defect distribution between the two regions, which leads to a difference in their maximum adsorption capacity. However, the overall evolution trends of the two are highly consistent, both showing the typical adsorption behavior of initial rapid growth and then approaching saturation. This result indicates that although there are certain differences in the microstructure of the two surface regions, which affect the absolute value of their saturation coverage, from the perspective of adsorption kinetics and adsorption mechanism, the adsorption process of water molecules on these two types of surfaces follows the same basic laws and exhibits consistent saturation characteristics. This further demonstrates that water adsorption is mainly controlled by the number of available sites on the surface, while the local structural differences are more reflected in the adsorption capacity rather than the essential mechanism of the adsorption process.

5.4.3 Anneal after adsorption

Without treatment

Fig.5.5 illustrates the time dependent evolution of the $\text{TiO}_2(110)-(1 \times 2)$ surface following water molecule adsorption. In the absence of any external treatment, the $\text{TiO}_2(110)-(1 \times 2)$ surface morphology was continuously monitored over a period of 10 hours. The observations show that throughout the entire duration, the sur-

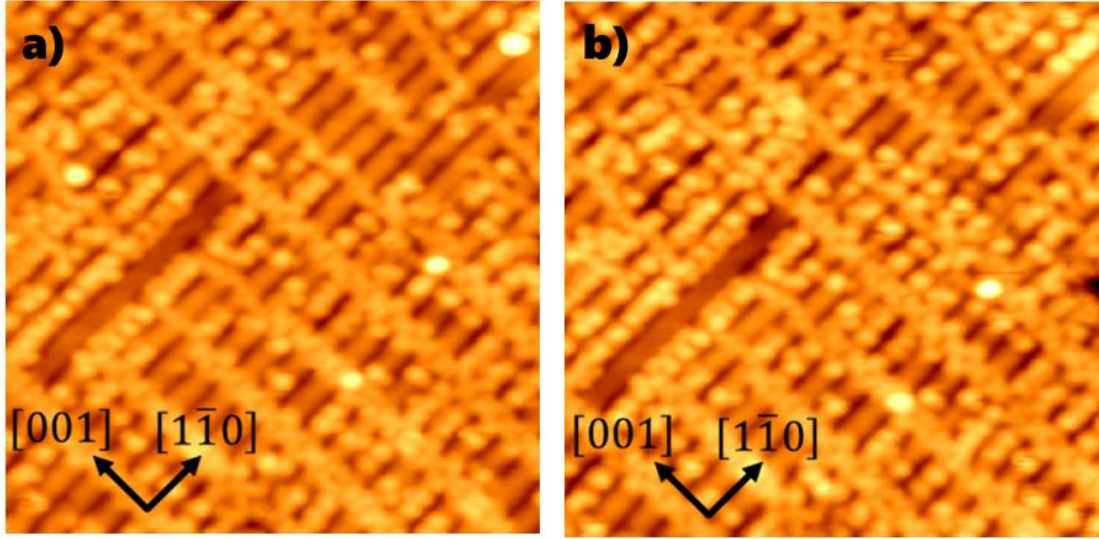


Figure 5.5: a) STM image of rutile $\text{TiO}_2(110)-(1 \times 2)$ water adsorbed surface without anneal. b) STM image of rutile $\text{TiO}_2(110)-(1 \times 2)$ water adsorbed after 10 hour without anneal. Tunneling current setpoint and sample bias voltage were 100 pA and 2.5 V, respectively. The scanning area is $30 \text{ nm} \times 30 \text{ nm}$.

face morphology remained essentially unchanged, with no obvious reconfiguration, disappearance of bright features, or emergence of new surface structures. These results indicate that simple water adsorption under ambient conditions is insufficient to induce significant structural rearrangement or morphological evolution of the $\text{TiO}_2(110)-(1 \times 2)$ surface. At the same time, the adsorbed water molecules remain on the surface and do not desorb under these conditions, suggesting a relatively stable water and $\text{TiO}_2(110)-(1 \times 2)$ interaction.

With annealing

As shown in Fig.5.6-a), when the surface was subsequently subjected to annealing at 450°C , the bright protrusion features observed previously under non-heated conditions gradually disappeared, while the previously partially obscured (1×2) reconstructed surface reappeared clearly. This phenomenon indicates that moderate thermal activation is conducive to the desorption of adsorbed species or the redistribution of them on the surface, thereby effectively restoring the original ordered structure of the $\text{TiO}_2(110)-(1 \times 2)$ surface. To further verify whether this process is solely caused by the thermal treatment itself, we conducted a comparative annealing experiment on the $\text{TiO}_2(110)-(1 \times 2)$ surface without introducing adsorbates at 450°C . The corresponding results are shown in Fig.5.6-c). Under this condition, the surface morphology did not undergo any significant changes, neither new connection structures were formed, nor was there any significant surface reconstruction. This comparative result clearly indicates that the 450°C annealing itself does not induce the formation of new link structures. The structural evolution observed previously in the composite system mainly results from the synergistic effect of adsorbates and thermal treatment, rather than a simple thermal effect.

Furthermore, significant structural changes were observed in the connection re-

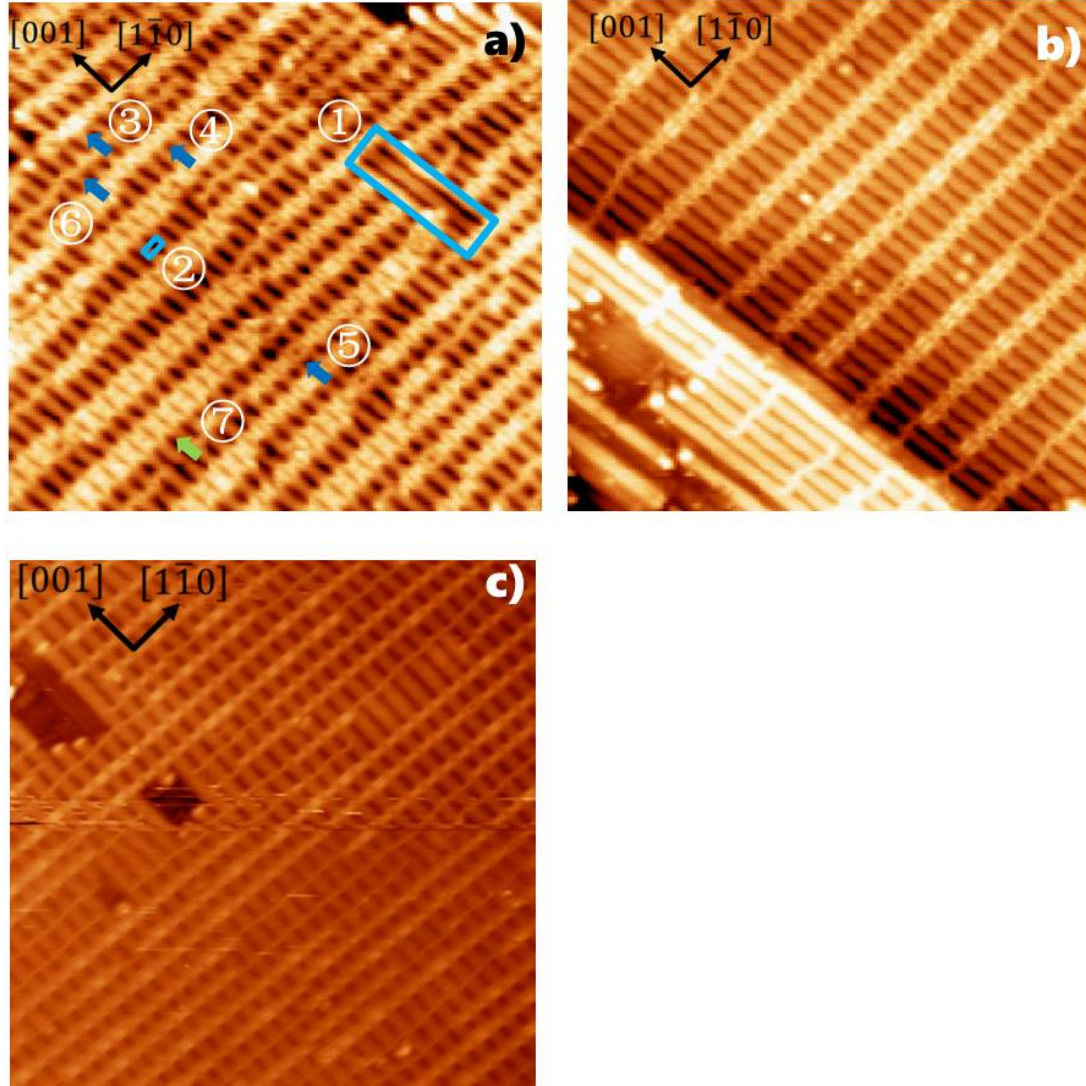


Figure 5.6: a) STM image of rutile $\text{TiO}_2(110)-(1 \times 2)$ water adsorbed surface with 450 °C anneal. 1. line defect, 2. (1×2) region, 3. = type, 4. X type, 5. O type, 6. single link, 7. double-cross-link b) STM image of rutile $\text{TiO}_2(110)-(1 \times 2)$ water adsorbed surface with 900 °C anneal after 450 °C anneal. c) STM image of $\text{TiO}_2(110)-(1 \times 2)$ without water adsorption and anneal with 450 °C. Tunneling current setpoint and sample bias voltage were 100 pA and 2.5 V, respectively. The scanning area is 30 nm $\times$ 30 nm.

gion. After a 450 °C annealing treatment, a new surface feature appeared on the TiO_2 surface, known as the double-cross-link structure. As shown in Fig.5.6-a), while the original various surface structures could still be clearly identified, a new connection structure (marked as 7 in the Fig.5.6-a)) was added to the surface, indicating that medium-temperature annealing can induce the occurrence of local surface reconstruction. However, this double-cross-link structure exhibited obvious thermal instability. When the annealing temperature was further increased to 900 °C, this structure completely disappeared, as shown in Fig.5.6-b). It is worth noting that 900 °C is the typical temperature at which highly ordered (1×2) surface reconstructions typically form on the TiO_2 surface, indicating that high-temperature annealing drives the surface to transform towards a thermodynamically more stable ordered structure, thereby eliminating intermediate or metastable structures.

5.5 Double-cross-link structure

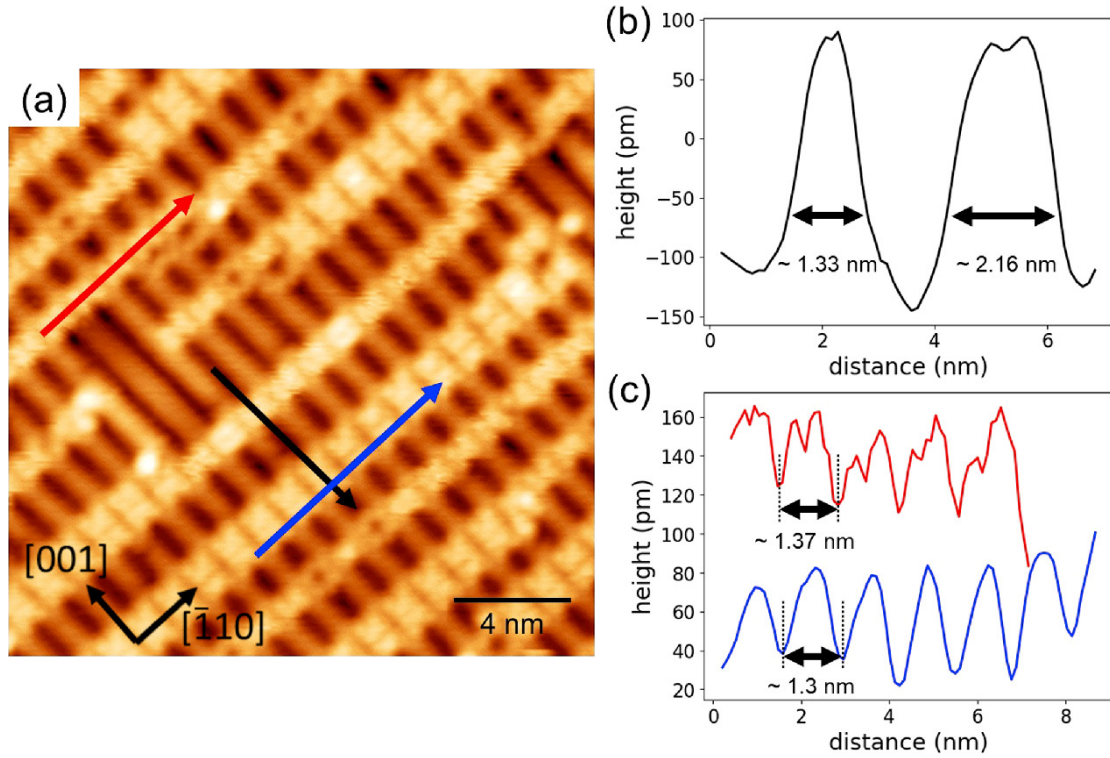


Figure 5.7: a) STM image of rutile $\text{TiO}_2(110)-(1 \times 2)$ water adsorbed surface annealed at 450 °C. b), c) line profiles on STM image shown in a). Tunneling current setpoint and sample bias voltage were 100 pA and 2.5 V, respectively. The scanning area is 30 nm $\times$ 30 nm.

In order to further analyze the double-cross-link, we scanned images with higher resolution. Fig.5.7 presents high resolution STM images and corresponding line profiles of the $\text{TiO}_2(110)-(1 \times 2)$ surface after water adsorption followed by annealing at 450 °C. The STM image in Fig.5.7-a) reveals the coexistence of multiple surface motifs, including the well established single link and double link structures

observed on the pristine (1×2) surface, as well as a newly formed, more extended structure.

A close-up examination of this new surface feature shows a morphology distinct from the previously known structures. Specifically, it appears as two adjacent double link units stacked along the $[001]$ direction, forming a bridged configuration that spans a larger surface area. For clarity and consistency, we refer to this feature as the double-cross-link structure in the remainder of this paper.

To quantitatively assess its geometric characteristics, a line profile analysis along the $[001]$ direction is shown in Fig.5.7-b). The measurement reveals that the length of the double-cross-link structure is approximately 1.6 times that of the conventional double link structure, while its height from the trough of the (1×2) surface remains essentially unchanged. This indicates that the structural extension occurs primarily in-plane, without inducing significant vertical distortion in the surface topography.

Further analysis in Fig.5.7-c) presents a line profile along the $[\bar{1}\bar{1}0]$ direction, which corresponds to the periodicity of the reconstructed surface rows. The pitch between adjacent double-cross-link structures is measured to be approximately 1.3 nm, which closely matches the periodicity of the underlying (1×2) asymmetric row structure. However, this pitch is slightly smaller than that of the conventional double link structure, suggesting that the formation of the double-cross-link motif may be accompanied by subtle in-plane compressive strain or lattice relaxation effects localized within the reconstructed rows.

The emergence of this new structural feature following water exposure and high-temperature annealing suggests a water-induced surface reconstruction process. The thermal energy likely facilitates surface atom mobility, enabling the reorganization of link structures into more energetically favorable or stabilized configurations under modified chemical potential conditions. These findings provide further insight into the dynamic restructuring behavior of the $\text{TiO}_2(110)-(1 \times 2)$ surface under reactive conditions and highlight the sensitivity of its morphology to water related processes.

To gain a more comprehensive and intuitive understanding of the influence mechanism of water molecule adsorption and thermal treatment on the evolution of the link structure of the $\text{TiO}_2(110)-(1 \times 2)$ surface, we conducted a systematic statistical analysis of the relative proportions of various link structures at different experimental stages. The relevant results are summarized in Fig.5.8. This statistics not only reflects the overall trend of the surface structure changes with processing conditions, but also provides a quantitative basis for identifying the key intermediate state structures. On the initially clean $\text{TiO}_2(110)-(1 \times 2)$ surface, the X type link is clearly dominant. This result is highly consistent with the general understanding in existing STM literature regarding this reconstructed surface. In this state, the distribution of surface link structures is relatively simple and stable, and no double-cross-link structures are observed. Therefore, this initial surface can be regarded as the thermodynamically stable reference state of the system under conditions without the interference of adsorbates, providing a clear reference for subsequent comparisons of the structural changes induced by different treatments. After the water molecules were exposed and subjected to low temperature annealing treatment, the distribution of surface link structures underwent a significant rearrangement. Statistical results indicated that the double-cross-link structure

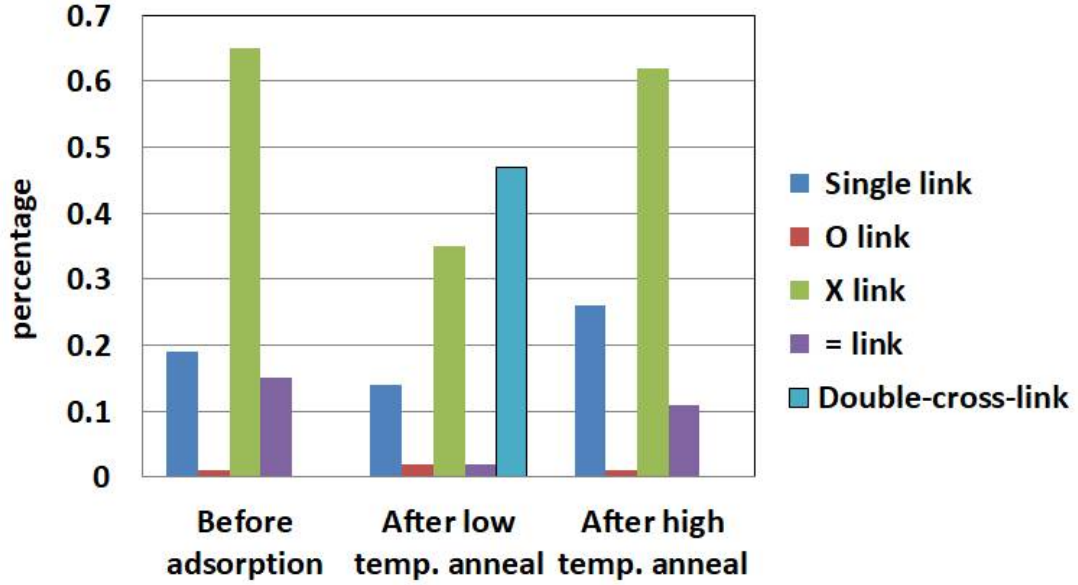


Figure 5.8: Statistics of $\text{TiO}_2(110)-(1 \times 2)$ structure obtained by annealing the $\text{TiO}_2(110)-(1 \times 1)$ surface at 900 °C, 450 °C anneal after water adsorption on $\text{TiO}_2(110)-(1 \times 1)$ surface and 900 °C anneal after that respectively

began to emerge and rapidly became an important new structural unit on the surface, with its proportion significantly increasing, indicating that this structure exhibited relatively high relative stability under these conditions. At the same time, the proportion of X type links decreased, but it remained a major component, suggesting that the original reconstituted framework was not completely destroyed. In contrast, the number of = type links significantly decreased, while O type links showed a certain degree of increase, although their overall proportion remained relatively low. This change in the distribution of link structures implies that the participation of water molecules may have altered the local chemical environment and surface chemical potential, thereby reducing the stability of some original link configurations and promoting the formation of new connection methods. When a further high-temperature annealing process is applied to the same surface that has undergone water treatment, the surface link structure undergoes another evolution. It is clearly that the double-cross-link structure completely disappears, while the link distribution gradually returns to a state highly similar to the initial clean surface: the X type link becomes the absolute dominant form again, the proportion of the = type link returns to the initial level, and the content of the O type link decreases once more. Based on the above results, it can be concluded that the formation of the double-cross-link structure is an reversible process induced by water-related surface activation and stabilized at a medium annealing temperature. The final distribution of the surface link structure is completely consistent with the classic $\text{TiO}_2(110)-(1 \times 2)$ reconstructed surface formed by direct high-temperature annealing through (1×1) phase. This result not only verifies the reversibility and metastable nature of the double-cross-link structure, but also further indicates that the $\text{TiO}_2(110)-(1 \times 2)$ surface still has significant structural recovery ability and reconfiguration resilience after undergoing complex

external conditions such as water adsorption and heat treatment, providing an important experimental basis for understanding its dynamic behavior in real reaction environments.

5.6 Discussion

The double-cross-link structure observed in this study was exclusively found on surfaces annealed at 450 °C following water adsorption, and was not present on either the clean or water-adsorbed surfaces. A previous study has demonstrated that on the $\text{TiO}_2(1 \times 1)$ surface, water molecules can adsorb at oxygen vacancy sites, effectively healing these point defects and leading to the oxidation of the surface[18, 28]. In contrast, for the (1×2) surface, no significant structural changes were observed after water adsorption at room temperature, suggesting that the reactions occurring on the (1×1) surface do not take place on this surface under these conditions. Consequently, it is reasonable to conclude that the link structure changes on the surface took place during the 450 °C annealing process. Therefore, it can be reasonably assumed that the change in the surface double-cross-link structure does not originate from the direct adsorption behavior of water at room temperature, but occurs during the subsequent 450 °C annealing process. At this temperature, the adsorbed water-related species may have higher reactivity, thereby interacting synergistically with the bridging structure on the (1×2) surface, promoting the adjustment of local bonding modes or atomic rearrangement. This process ultimately drives the formation of a new cross link structure, which does not occur under the annealing conditions of a clean surface.

Previous temperature-programmed desorption (TPD) studies on the $\text{TiO}_2(110)$ surface have revealed peaks corresponding to water desorption from the water adsorbed surface near room temperature and around 250 °C[29, 30]. This indicates that water molecules and the hydroxyl groups formed by their dissociation can undergo desorption or recombination at relatively low temperatures. From this, it can be inferred that the hydrogen atoms contained in the hydroxyl groups are difficult to stably exist on the surface within the higher temperature range, and thus are less likely to participate in the surface reaction process observed at 450 °C during the annealing process. Our experimental results further support the view that, during the high-temperature annealing process, the dominant factor is not the direct involvement of hydroxyl groups, but rather the decomposition of water molecules.

The changes in surface structure observed after annealing at different temperatures reveal the complex interaction between adsorbed water-related species and the $\text{TiO}_2(110)$ surface. The formation of the double-cross-link structure after annealing at 450 °C indicates that the adsorbed species influence the surface reconstruction process. When this surface was further annealed at 900 °C, instead of reverting to a complete $\text{TiO}_2(1 \times 2)$ structure, a mixture of $\text{TiO}_2(1 \times 1)$ surfaces and disordered regions was observed. This observation aligns with previous findings by Ojima. et al[19], who reported that annealing the $\text{TiO}_2(1 \times 2)$ surface at 600 °C in an oxygen atmosphere leads to a $\text{TiO}_2(1 \times 1)$ structure formation with partially disordered areas. This further indicates that during the 450 °C annealing process, water molecules are highly likely to decompose, resulting in the

surface being in a weak oxygen environment. The research conducted by M. Li et al. on introducing oxygen to fill the surface oxygen vacancies also to some extent supports this conclusion[31].

Based on these considerations, it is reasonable to propose that the double-cross-link structure formed under low-temperature annealing conditions is associated with the decomposition of water molecules and their subsequent interaction with the surface. Water molecules can undergo partial dissociation on reactive surfaces, inducing local structural rearrangements and modifying the surface chemical environment. In the context of link region formation, the direct participation of hydroxyl species appears to be limited, as the typical formation of link structures is generally not accompanied by detectable hydrogen-related effects. This observation suggests that hydrogen is unlikely to play a dominant role during the link formation process. Instead, surface-assisted decomposition processes may occur, leading to the generation of a weakly oxidizing environment that promotes structural reorganization and stabilizes the resulting double-cross-link configuration. Such a mechanism is consistent with reported surface evolution pathways driven by energy minimization and local chemical interactions, although further experimental verification is required.

Based on these observations and previous studies, we propose a mechanism for the observed structural changes. During the annealing process, the adsorbed substances related to water undergo decomposition into water molecules, leaving behind the remaining oxygen atoms. These oxygen atoms cause the surface to oxidize. This oxidation process drives the structural changes observed at moderate temperatures such as 450 °C. Further investigations using complementary techniques, such as spectroscopy and theoretical calculations, could provide deeper insights into the energetics and mechanisms of these surface processes.

Notably, the double-cross-link structure exhibits a different periodicity in the $[1\bar{1}0]$ direction compared to the conventional bridging structure, indicating that it induces stress in the in-plane direction. This stress is expected to alter the electronic state of the surface, potentially influencing photocatalytic reactions like the anatase $\text{TiO}_2(001)$ surface case[32]. Although investigating this aspect is beyond the scope of the present study, the possibility of tuning photocatalyst performance through in-plane stress suggests that our findings could serve as a valuable reference in the surface design and control of photocatalysts.

5.7 Summary

In this study, we systematically investigated the adsorption behavior of water molecules on the rutile $\text{TiO}_2(110)-(1 \times 2)$ surface and the induced surface structure evolution process by using STM. The experimental results show that a large number of bright features can be observed on the surface after water adsorption, which can be attributed to the adsorption of water molecules or their dissociation products on the surface. However, compared with the clean $\text{TiO}_2(110)-(1 \times 2)$ surface, the overall reconstruction period and atomic level structure of the substrate surface remain basically unchanged, indicating that the adsorption of water molecules at room temperature does not significantly disrupt or rearrange the original surface reconstruction structure. This result indicates that the adsorption of

water molecules is molecular adsorption, and at the same time, water adsorption mainly occurs at local active sites.

Furthermore, when the water-adsorbed samples were annealed at 450 °C, we observed in the STM images a novel bridging structure that had not previously appeared on the clean surface or only on the water-adsorbed surface. This paper refers to it as the double-cross-link structure. This structure shows a distinct periodic arrangement along the $[1\bar{1}0]$ crystal direction, and its period is slightly less than twice that of the X type structure. This might be because this novel link has a certain strain effect in the surface plane, which may affect the surface structure. Based on the existing literature reports and the analysis of the experimental results of this work, we further propose that the formation of this double-cross-link structure is closely related to the water decomposition and the surface oxidation process involving OH groups during the annealing process. Specifically, water molecules adsorb on the surface and partially dissociate. Under high temperature annealing conditions, they may react with surface Ti or defect sites, promoting the reconstruction of the local oxygen coordination environment and ultimately inducing the formation of this stable novel bridging structure. This result not only reveals that water molecules not only exist as adsorbed species on the $\text{TiO}_2(110)-(1 \times 2)$ surface, but also can deeply participate in the surface reconstruction process under thermal activation conditions. It also provides a new experimental basis for understanding the surface structure evolution of TiO_2 and its catalytic performance regulation mechanism with water participation.

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Chapter 6

Conclusion and prospect

6.1 Conclusion

In this work, we systematically investigated the structural and adsorption properties of the $\text{TiO}_2(110)-(1 \times 2)$ surface by combining STM experiments and DFT simulations. The single link structure based on the asymmetric (1×2) model was validated through high consistency between simulated and experimental STM images and total energy comparisons, confirming its stability and rationality. Building on this, three typical double link structures were constructed and analyzed. Their formation mechanisms were primarily governed by the relative orientation of single strands, local atomic positions, and the presence of vacancies, which together determine the type of double link, surface coverage, and local electronic structures. The simulated STM images of these double link structures showed excellent agreement with experimental observations, demonstrating the reliability of the proposed models.

Verification and stability analysis of link structure

A systematic investigation of link structures on the $\text{TiO}_2(110)-(1 \times 2)$ surface reveals a unified atomic-level formation mechanism governing both single link and double link configurations. The single link structure based on the asymmetric (1×2) model is confirmed to be energetically stable and structurally reasonable through consistent STM observations and DFT total energy comparisons, establishing it as a fundamental and reliable structural unit of the link region. Building upon this validated single link model, representative double link structures are identified and shown to originate from specific combinations of neighboring single links. Their formation is primarily determined by the relative orientation of the single strands, local atomic configurations, and the presence of vacancies, which collectively control the resulting double link type. These findings clarify the intrinsic relationship between single and double link structures and establish clear atomic-scale formation rules for link region evolution on the $\text{TiO}_2(110)-(1 \times 2)$ surface. These results provide a solid foundation for further investigations into surface adsorption processes, defect-related reactivity, and catalytic mechanisms on the $\text{TiO}_2(110)-(1 \times 2)$ surface.

Adsorption of water molecules and surface structure evolution

A systematic study was conducted on the adsorption behavior of water molecules on the $\text{TiO}_2(110)-(1 \times 2)$ surface. The results showed that at room temperature, water molecules mainly existed in the form of molecular adsorption and preferentially adsorbed in the (1×2) region. After low-temperature annealing treatment, a double-cross-link structure could be formed on the surface; while after further increasing the annealing temperature, this structure would gradually disappear and the surface would return to its original configuration, indicating the reversibility of this structure formation. Based on the aforementioned analysis of the link structure, it can be concluded that the link region is mainly composed of titanium and oxygen atoms. Therefore, the surface structure changes caused by the adsorption of water molecules are mainly related to the partial dissociation behavior of water molecules under thermal excitation conditions. In a weak oxygen environment, the oxygen provided by the decomposition of water molecules can participate in the rearrangement of surface atoms, thereby inducing the formation of a new link. Thus, it can be inferred that the adsorption process of water molecules on the $\text{TiO}_2(110)-(1 \times 2)$ surface follows an evolutionary path of first molecular adsorption and then dissociation under increased energy conditions. This conclusion provides an important basis for understanding the role of water molecules in the surface reconstruction of $\text{TiO}_2(110)-(1 \times 2)$ and their regulation of local structural stability and reactivity. It also lays an experimental and theoretical foundation for further research on surface adsorption, reaction kinetics, and catalytic mechanisms.

Overall, this study demonstrates that a comprehensive understanding of the $\text{TiO}_2(110)-(1 \times 2)$ single link and double link structures provides an atomic-level foundation for in-depth analysis of water molecule adsorption behavior. Water molecules not only exist in molecular adsorption form but also participate in the surface reconstruction process, and their behavior is significantly influenced by the arrangement of surface atoms and the local environment. This research offers important references for further exploration of water and surface interactions, electronic state regulation, and optimization of photocatalytic activity.

6.2 Prospect

Looking forward, future studies could focus on the rational design and modification of $\text{TiO}_2(110)$ surfaces to optimize water adsorption. Detailed analysis of adsorption dynamics, dissociation pathways, and interactions with defect sites will deepen understanding of surface behavior. Integrating these insights with photocatalytic performance studies can guide the development of more efficient TiO_2 -based catalysts and enable precise control of reaction sites, advancing water-splitting and other photocatalytic applications.

Directional design and surface regulation

Based on the understanding of the atomic configuration, formation mechanism, and role of the link structure on the $\text{TiO}_2(110)-(1 \times 2)$ surface in the adsorption process obtained from this study, future research can further focus on the

directional design and fine regulation of the $\text{TiO}_2(110)$ surface. By controlling the arrangement of surface atoms, the defects, and link types, it is expected to achieve controllable regulation of the density and configuration of the surface link structure, thereby systematically changing the local geometric structure and electronic properties of the surface. Existing results indicate that the link structure may serve as an important active site in surface reactions, especially having potential promoting effects in reactions such as organic molecule decomposition. Therefore, in the future, attempts can be made to control surface growth through annealing conditions or other methods to achieve directional generation, saturated distribution, or selective inhibition of the link structure, in order to construct surface structures with higher density of active sites or specific reaction selectivity. At the same time, by regulating the presence and disappearance of the link structure, it is expected to achieve regulation of the local electronic structure of the surface and even the effective energy gap, thereby establishing a quantitative correlation between surface structure, electronic properties, and reaction activity.

Water adsorption mechanism and photocatalytic applications

Based on the observation in this study that water molecules on the $\text{TiO}_2(110)-(1 \times 2)$ surface may dissociate under low-temperature conditions, future research can further explore the potential application value of this surface in water decomposition reactions. By introducing additional energy input methods, such as ultraviolet light, the possibility of promoting the dissociation of water molecules at room temperature can be explored.

Research outputs

Paper

1. Li, F., Katsube, D., Diao, Z., Yamashita, H., Abe, M. (2025). STM study of unusual link structure formation on rutile $\text{TiO}_2(110)-(1 \times 2)$ surface induced by water adsorption and low-temperature annealing. *Physica Scripta* (Published 16 July 2025)
2. Li, F., Diao, Z., Yamashita, H., Tohei, T. Abe, M. (2025). Structural Model for Single Links of $\text{TiO}_2(110)-(1 \times 2)$ Surface from Analyses of Scanning Tunneling Microscopy and Density Functional Theory Calculations. *Japanese Journal of Applied Physics* (submitted)
3. Li Fengxuan et al., Structural Model for Double Links of $\text{TiO}_2(110)-(1 \times 2)$ Surface and their relationship studies by Scanning Tunneling Microscopy and Density Functional Theory Calculations (in preparation)
4. Zhuo Diao, Keiichi Ueda, Linfeng Hou, Fengxuan Li, Hayato Yamashita, Masayuki Abe, “AI-equipped scanning probe microscopy for autonomous site-specific atomic-level characterization at room temperature”, *Small Methods*, 2400813 (2024).
5. D. Katsube, S. Ohno, S. Takayanagi, S. Ojima, M. Maeda, N. Origuchi, A. Ogawa, N. Ikeda, Y. Aoyagi, Y. Kabutoya, K. Kim, L. Hou, F. Li, Y. Tsuda, H. Yoshida, S. Nishi, T. Sakamoto, E. Inami, A. Yoshigoe, and M. Abe: “Oxidation of Anatase $\text{TiO}_2(001)$ Surface Using Supersonic Seeded Oxygen Molecular Beam”, *Langmuir* Vol.37, 12313(2021)

Conference

1. Eiichi Inami, Seiga Koga, Linfeng Hou, Fengxuan Li, Daiki Katsube, and Masayuki Abe, Atomic-Scale Insights into Electronic States of Microfacets on Rutile $\text{TiO}_2(001)$ Surface, Annual Meeting of the Japan Society of Vacuum and Surface Science 2024, October 20–24, 2024, Kitakyushu International Conference Center, Kitakyushu, Japan, 5P02.
2. Fengxuan Li, Daiki Katsube, Zhuo Diao, Hayato Yamashita, and Masayuki Abe, In-situ Imaging of Water Adsorption Processes and Their Effects on the $\text{TiO}_2(110)-(1 \times 2)$ Surface, 37th International Microprocesses and Nanotechnology Conference (MNC 2024), November 12–15, 2024, Kyoto Brighton Hotel, Kyoto, Japan, 13D-4-1 (16:30).
3. Zhuo Diao, Zijie Meng, Fengxuan Li, Linfeng Hou, Tetsuya Tohei, Masayuki Abe, and Akira Sakai, Anchor Point-Based Image Registration Method for Microscope Topographic Map Structure Analysis, 37th International Microprocesses and Nanotechnology Conference (MNC 2024), November 12–15, 2024, Kyoto Brighton Hotel, Kyoto, Japan, 14P-1-63.

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4. Daiki Katsube, Tatsuya Yokoi, Eiichi Inami, Fengxuan Li, Katsuyuki Matsunaga, and Masayuki Abe, Study of Line Defects on Rutile $\text{TiO}_2(110)-(1 \times 2)$ Surfaces by Non-Contact Atomic Force Microscopy, The 71st Spring Meeting of the Japan Society of Applied Physics, March 15–18, 2023, Tokyo City University, Setagaya Campus, Tokyo, Japan, 23p-12G-4.
 5. Daiki Katsube, Tatsuya Yokoi, Eiichi Inami, Fengxuan Li, Katsuyuki Matsunaga, and Masayuki Abe, Non-Contact Atomic Force Microscopy Study of Line Defects on Rutile $\text{TiO}_2(110)-(1 \times 2)$ Reconstructed Surfaces, Annual Meeting of the Japan Society of Vacuum and Surface Science 2023, October 31 – November 2, 2023, Nagoya Congress Center, Aichi, Japan, 2Bp04.
 6. Daiki Katsube, Shinya Ohno, Shuhei Takayanagi, Akiteru Ojima, Motoyasu Maeda, Naoki Origuchi, Arata Ogawa, Natsuki Ikeda, Yoshihide Aoyagi, Yuito Kabutoya, Kyungmin Kim, Linfeng Hou, Fengxuan Li, Yasutaka Tsuda, Hikaru Yoshida, Shizuka Nishi, Tetsuya Sakamoto, Eiichi Inami, Akitaka Yoshigoe, and Masayuki Abe, X-ray Photoelectron Spectroscopy Study of Anatase $\text{TiO}_2(001)$ Surfaces Irradiated with a Supersonic Molecular Beam, The 69th Spring Meeting of the Japan Society of Applied Physics, Aoyama Gakuin University, Sagamihara Campus, Japan, 26p-E206-2.
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 9. Fengxuan Li, Daiki Katsube, Eiichi Inami, Hayato Yamashita, and Masayuki Abe, In-situ Scanning Tunneling Microscopy Observation of Water Adsorption on Rutile $\text{TiO}_2(110)-(1 \times 2)$ Surfaces, The 81st Autumn Meeting of the Japan Society of Applied Physics, September 8–11, 2020, Online, 11a-Z06-10.
 10. Fengxuan Li, Daiki Katsube, Eiichi Inami, Hayato Yamashita, and Masayuki Abe, In-situ Observation of Water Adsorption on Rutile $\text{TiO}_2(110)-(1 \times 2)$ Surfaces at Room Temperature by Scanning Tunneling Microscopy, 33rd International Microprocesses and Nanotechnology Conference (MNC 2020), September 12, 2020, Online.
 11. Fengxuan Li, Masayuki Abe, Hayato Yamashita, Daiki Katsube, and Eiichi Inami, Water Adsorption Measurements on $\text{TiO}_2(110)-(1 \times 2)$ Surfaces Using Non-Contact Atomic Force Microscopy and Scanning Tunneling Microscopy, 33rd Fall Meeting of the Ceramic Society of Japan, September 2–4, 2020, Online, 2C08.

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Appendix A

KPOINTS

Automatic mesh

0

Gamma

1 1 1

0. 0. 0.

Appendix B

INCAR (for optimizing)

```
PREC      = Normal
ENCUT     = 330
IBRION    = 2
NSW       = 100
ISIF      = 2
NELMIN    = 4
EDIFF     = 5.0e-06
EDIFFG    = -0.5
VOSKOWN   = 1
NBLOCK    = 1
NELM      = 100
ALGO      = Normal (blocked Davidson)
ISPIN     = 1
INIWAV    = 1
ISTART    = 0
ICHARG    = 2
LWAVE     = .FALSE.
LCHARG    = .FALSE.
ADDGRID   = .FALSE.
ISMear    = 0
SIGMA     = 0.1
LREAL     = .TRUE.
RWIGS     = 1.45 0.73
```

Appendix C

INCAR (for WAVECAR)

```
PREC = Normal
ENCUT = 330
IBRION = -1
NSW = 0
ISIF = 4
NELMIN = 4
EDIFF = 1.0e-05
EDIFFG = -0.5
VOSKOWN = 1
NBLOCK = 1
NELM = 100
ALGO = Normal (blocked Davidson)
ISPIN = 1
INIWAV = 1
ISTART = 0
ICHARG = 2
LWAVE = .TURE.
LCHARG = .TURE.
ADDGRID = .FALSE.
ISMEAR = 0
SIGMA = 0.1
LREAL = .TRUE.
RWIGS = 1.45 0.73
```

Appendix D

INCAR (for simulation)

```
SYSTEM = PAR

PREC = Normal
ENCUT = 330
IBRION = -1
NSW = 0
ISIF = 4
NELMIN = 4
EDIFF = 1.0e-05
EDIFFG = -0.5
VOSKOWN = 1
NBLOCK = 1
NELM = 100
ALGO = Normal (blocked Davidson)
ISPIN = 1
INIWAV = 1
ISTART = 1
LWAVE = .TURE.
LCHARG = .TURE.
LPARD = .TURE.
NBMOD = -3 ; EINT = 1.6
LSEPB = .FALSE.
LSEPK = .FALSE.
ADDGRID = .FALSE.
ISMear = 0
SIGMA = 0.1
LREAL = .TRUE.
RWIGS = 1.45 0.73
```