Surface and Interface Engineering in Semiconducting Electrocatalyst and Photo(electro)catalyst

Haifeng Feng
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UNIVERSITY OF WOLLONGONG

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Surface and Interface Engineering in Semiconducting

Electrocatalyst and Photo(electro)catalyst

This thesis is presented as part of the requirements for the

Award of the Degree of

Doctor of Philosophy

from the

University of Wollongong

by

HAIFENG FENG

B. Sc., M. Sc.

Supervisors:

Dr. Yi Du, Dr. Xun Xu, Prof. Shi Xue Dou

Institute for Superconducting and Electronic Materials

Faculty of Engineering

July 2018
# Table of contents

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1.1 General background</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1.2 Literature review and research motivation</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>1.2.1 Semiconductor electrocatalysts</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>1.2.2 TiO$_2$ based catalysts</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>1.2.3 Semiconductor photocatalyst and photo(electro)catalysts</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>1.2.4 BiOBr based catalysts</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>1.3 Outline of chapters</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>1.4 References</td>
<td>18</td>
</tr>
<tr>
<td>2</td>
<td>Experimental Techniques</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>2.1 Scanning tunneling microscopy</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>2.1.1 Quantum tunneling</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>2.1.2 Working principle of STM</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>2.1.3 Ultra-high vacuum system and molecular beam epitaxy</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>2.2 Atomic force microscopy</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>2.2.1 Working principles of AFM</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>2.2.2 Working modes of AFM</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>2.3 Other facilities</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>2.3.1 Scanning electron microscopy and focused ion beam</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>2.3.2 Transmission electron microscopy</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>2.3.3 Photoelectron spectroscopy</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>2.4 References</td>
<td>49</td>
</tr>
<tr>
<td>3</td>
<td>Characterization of TiO$_2$(110) surface by STM</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>3.1 Introduction</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>3.2 Experimental section</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>3.3 Results and discussion</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>3.3.1 Rutile(110) surface with (1×1) reconstruction</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>3.3.2 OV point defects on (1×1) surface</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>3.3.3 Rutile(110) surface with (1 × 2) reconstruction</td>
<td>56</td>
</tr>
</tbody>
</table>
Appendix A: List of publications ................................................................. 139
Appendix B: Conference contributions .................................................... 141
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At last, I want to take this opportunity of thanks my parents and my wife for their endless love and support during this four years.
Certification

I, Haifeng Feng, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Institute for Superconducting & Electronic Materials, Faculty of Engineering, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for qualifications at any other academic institution.
List of abbreviations

HER  hydrogen evolution reaction
OER  oxygen evolution reaction
LDOS local density of states
TMO  transition metal oxide
XAS  x-ray absorption spectroscopy
STM  scanning tunneling microscopy
STS  scanning tunneling spectroscopy
DFT  density functional theory
AFM  atomic force microscopy
KPFM kelvin probe force microscopy
SKPM scanning kelvin probe microscopy
CPD  contact potential difference
UHV  ultra-high vacuum
TMP  turbo molecular pump
TSP  titanium sublimation pump
MBE  molecular beam epitaxy
LT  low temperature
GV  gate valve
SEM  scanning electron microscopy
FIB  focused ion beam
EDX  energy-dispersive x-ray spectroscopy
TEM  transmission electron microscopy
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAED</td>
<td>selected area electron diffraction</td>
</tr>
<tr>
<td>HRTEM</td>
<td>high resolution transmission electron microscopy</td>
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<tr>
<td>STEM</td>
<td>scanning transmission electron microscopy</td>
</tr>
<tr>
<td>ABF</td>
<td>annular bright-field</td>
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<tr>
<td>HAADF</td>
<td>high angle annular dark-field</td>
</tr>
<tr>
<td>EELS</td>
<td>electron energy loss spectroscopy</td>
</tr>
<tr>
<td>GPA</td>
<td>geometric phase analysis</td>
</tr>
<tr>
<td>XPS</td>
<td>x-ray photoelectron spectroscopy</td>
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<tr>
<td>UPS</td>
<td>ultraviolet photoelectron spectroscopy</td>
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<td>UV</td>
<td>ultraviolet</td>
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<tr>
<td>UV-vis</td>
<td>ultraviolet-visible</td>
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<td>CB</td>
<td>conduction band</td>
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<td>VB</td>
<td>valence band</td>
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<tr>
<td>CBM</td>
<td>conduction band maximum</td>
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<td>VBM</td>
<td>valence band maximum</td>
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<td>OV</td>
<td>oxygen vacancy</td>
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<td>OHP</td>
<td>hydroxyl group pairs</td>
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<td>CNT</td>
<td>carbon nanotube</td>
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<tr>
<td>MO</td>
<td>methyl orange</td>
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<td>Rh B</td>
<td>rhodamine B</td>
</tr>
<tr>
<td>CTAB</td>
<td>cetyl trimethylammonium bromide</td>
</tr>
<tr>
<td>FFT</td>
<td>fast Fourier transform</td>
</tr>
<tr>
<td>XRD</td>
<td>x-ray diffraction</td>
</tr>
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<td>PPMS</td>
<td>physical property measurement system</td>
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<td>VASP</td>
<td>vienna Ab initio simulation package</td>
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<tr>
<td>Acronym</td>
<td>Term</td>
</tr>
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<td>---------</td>
<td>-------------------------------------------</td>
</tr>
<tr>
<td>GGA</td>
<td>generalized gradient approximation</td>
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<td>PBE</td>
<td>Perdew-Burke-Ernzerhof</td>
</tr>
<tr>
<td>PAW</td>
<td>projector augmented wave</td>
</tr>
<tr>
<td>ZPE</td>
<td>zero point energies</td>
</tr>
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<td>LSV</td>
<td>linear sweep voltammetric</td>
</tr>
<tr>
<td>EASA</td>
<td>electrochemically active surface area</td>
</tr>
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<td>RHE</td>
<td>reversible hydrogen electrode</td>
</tr>
</tbody>
</table>
Abstract

Surface and interface engineering is one of the most effective approaches in tuning semiconductors for their chemistry (energy, environment and catalysis) and device applications (electronic devices, and optical-electronic devices).

In this thesis, we show several approaches of modifying the catalytic and electronic properties of several semiconductors through manipulating their surface and interface. Techniques including scanning probe microscopies (SPM), electron microscopies, and electron spectroscopies, and, X-ray spectroscopies, were taken used to characterize the effect of surface and interface engineering, and the effect on their electronic properties. This thesis includes:

1. Oxygen vacancies (OV) engineering on TiO$_2$ rutile(110) single crystal. By carefully controlling the annealing temperature and annealing time, OV defects can be precisely introduced into the single crystal. The evolution of the surface structure was investigated by in-situ low temperature STM. It was found that at 900 K, OV point defects isolating with each other exist on the (1 × 1) surface. In addition, OV in the surface tended to be filled either water molecule or OHS. When the annealed temperature increased to 1300 K, (1 × 2) surface reconstruction dominated on the surface, in which cross-links defects caused by more oxygen deficiency were found.

2. Activating TiO$_2$ for electrocatalysis by surface vacancy engineering. STEM techniques clarified that the good crystalline nature of reduced TiO$_2$ with and the spatial distribution of OV in the surface and near-surface region. A mid-gap defect electronic state was created by the OV, which can effective enhance the electric conductivity of the reduced TiO$_2$. The reduced TiO$_2$ exhibit tremendous enhancement in hydrogen
evolution reaction (HER) due to the increased electric conductivity and amounts of active sites. Combing the in-situ observation of the water splitting reaction by STM and DFT calculations, subsurface oxygen vacancies and low coordinated Ti ions (Ti$^{3+}$) demonstrated their roles in enhancing the electrical conductivity and promoting electron transfer and hydrogen desorption, which activate reduced TiO$_2$ single crystal in the hydrogen evolution reaction in alkaline media. This study offers a rational route for developing reduced transition metal oxide for low-cost and highly active hydrogen evolution reaction catalysts, to realize over all water splitting in alkaline media.

3. The band structure of BiOBr 2D nanosheets was tuned by the strain for photocatalysis. The inner strain in the BiOBr nanosheets has been tuned continuously by controlled manipulating their shapes. The photocatalytic performance of BiOBr in dye degradation can be manipulated by the strain effect. The low-strain BiOBr nanosheets show improved photocatalytic activity. DFT suggest that strain can modify the band structure and symmetry in BiOBr. The enhanced photocatalytic activity in low-strain BiOBr nanosheets is due to improved charge separation attributable to a highly dispersive band structure with an indirect band gap.

4. Constructing two dimensional (2D) lateral pseudo-heterointerface by strain engineering in BiOBr nanosheets. Taking advantage of their strain-sensitive layer structure, 2D lateral pseudo-heterogeneous interface are realized in the single-component BiOBr nanosheets by finely tune the pH value in synthesis. Due to the proper band alignment cross the interface, charge separation under visible light irradiation was enhanced, which was reflected by the photo-current measurements and the degradation experiments of pollutions. The strain engineering was demonstrated to
be an effective way to tune the electronic structure of BiOBr and promote its efficiency in photoenergy conversion applications. In addition, the construction of the lateral pseudo-heterostructure through strain exhibit promising applications in building unprecedented 2D systems with exciting properties.
Chapter 1 Introduction

1.1 General background

Semiconducting electronic materials can be defined as the semiconductors which are applied for their electrical properties. According to band theory, a semiconductor material with small but non-zero band gap, has an electric conductivity between that of an insulator and that of most metals. The behaviours of electrons in semiconductors are determined by their band structure, which has been successfully implemented in describing many physical properties of solids. They have been utilized in a variety of application fields mainly based on their different electronic properties, including chemistry (energy conversion and storage, environmental remediation and catalysis) and device applications (electronic devices, and optical-electronic devices).\[1-2\]

Surface and interface plays a critical role in determining the electronic properties of semiconductor materials, especially for those in nanostructures with very large specific surface area.\[3-5\] Abundant surface mismatches, low coordinated ions or atoms, and surface defects can strongly alter their electronic structures, which could play a vital role in the corresponding performances in their applications.\[6-8\] However, effectively characterizing conditions of surface or interface, and modifying the electronic properties through controllably manipulating surface conditions are challenging, due to the lack of approaches in monitoring fine surface structure and localized variation of electronic structure in micro or nano-scale. Effectively control the species, concentration, and distributions of surface defects and their effects on the electronic structure, hence, are of great significance in developing their applications.
1.2 Literature review and research motivation

1.2.1 Semiconductor electrocatalysts

In the research filed of energy conversion, including fuel cells, solar cells and batteries, electrocatalysts are crucial in the reaction rate, efficiency, and selectivity.\textsuperscript{[9]} Pursuing efficient and low-cost electrocatalysts is one of the key topics in this filed. In this thesis, we will largely limit the introduction to water electrolysis that split water into hydrogen and oxygen. For both the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), noble metal (Pt, Ir, Au) or noble metal based electrocatalysts with high activity and stability are still dominating in these applications, which are not desirable due to their high cost and low-abundance.

Varieties of earth-abundant semiconductor materials have been extensively explored as alternatives of noble metal based electrocatalysts, in which the most efficient ones are designed based on transition metal elements (Fe, Co, Ni, Cu, Mo, W, Mn, Ti, Zn) and $p$-block elements (S, Se, C, O, N, P).\textsuperscript{[10-16]} Among them, transitional metal oxides (TMOs), which are being widely applied either as catalysts or supports in industrial processes, have been recognized as appealing alternatives to noble-metal based electrocatalysts for the OER, especially in alkaline media.\textsuperscript{[17-19]}

To reach a high electrocatalytic activity close to noble metals, two requirements are needed to be met in the first place. The first one is a high conductivity, which enable the transport of electrons between electrodes and active sites. To overcome the poor conductivity of common semiconductor materials, conductive materials, for examples carbon based materials, such as, carbon based materials and Ni foams, are need to be used as conducting substrate to fabricate a heterogeneous structure.\textsuperscript{[20-22]}
Figure 1.1 (a) Trend in overpotential for the OER is shown as a function of the 3d transition elements. (b) Trend in overpotential for the HER is shown as a function of the 3d transition elements. In both reactions, the trends of Mn < Fe < Co < Ni was determined.[23] Reproduced with permission from Springer Nature.

The second important aspect is the active site on the surface of an electrocatalyst, in which the catalytic charge transfer happens. Identifying the active site of high active electrocatalysts are important in further improving their activity, revealing the catalytic mechanism and rationally developing new electrocatalysts. For example, for an early work shown in Figure 1.1, combined with X-ray absorption spectroscopy (XAS),
scanning tunneling microscopy (STM) and electrochemical measurements, Subbaraman et al. proposed that the strength of OH-M$^{2+δ}$ (0 ≤ δ ≤ 1.5) energetic (M, Ni < Co < Fe < Mn) play the determining role in the reactivity of both OER and HER in alkaline media (Mn < Fe < Co < Ni), which was helpful for guiding further designing electrocatalysts by tuning active sites.[23]

Inspired by these works, intense attempts have been made in developing TMOs for HER and overall water splitting in recent years. Nanoscale NiO/Ni-carbon nanotube (CNT) material[24], Ni/CoO$_2$–CNT[25], 3D crystalline/amorphous Co/Co$_3$O$_4$ core/shell nanostructure on Ni foam[26], oxygen vacancy (OV)-CoO/carbon[27] and TiO$_2$ nanodots/Co nanotubes on carbon fibers[28] have exhibited competitive HER activities toward commercial Pt/C catalysts in alkaline media. Hollow Co$_3$O$_4$ microtube arrays on nickel skeleton,[29] porous MoO$_2$ nickel foam,[30] Ni–Co–A (A = P, Se, O) nanosheets on nickel foam[31] and have been reported to be highly active bifunctional electrocatalysts for overall water splitting.

1.2.2 TiO$_2$ based catalysts

![The crystal structure of the three phases of TiO$_2$.](image)

Figure 1.2 The crystal structure of the three phases of TiO$_2$. (a) anatase (tetragonal, a = 0.3785 nm, c = 0.9513 nm), (b) rutile (tetragonal, a = 0.4593 nm, c = 0.2959 nm), (c) brookite (orthorhombic, a = 0.5455 nm, b = 0.9181 nm, c = 0.5142 nm).

TiO$_2$ is found exist in nature in three crystal structures.[38] The crystal structure of the three phases is shown in Figure 1.2. Rutile, a tetragonal structure, is the most
common one in nature with the most stable structure. Due this reason, rutile is the most studied oxide surface although in the two decades.\textsuperscript{[32]} Beside rutile, anatase is also tetragonal structure, while brookite is orthorhombic. In recent years, the study of anatase in fields of both surface characterization and surface catalysis have also got huge progresses.\textsuperscript{[33-37]}

In the study of catalytic properties of TiO\textsubscript{2}, rutile(110) face is mostly selected, because it is the most thermodynamically stable crystal face of TiO\textsubscript{2}. The information and knowledge we got from this surface are also useful for the understanding of other crystal faces and phases of TiO\textsubscript{2}, as well as other oxide surfaces. As shown in Figure 1.2 (a), rutile TiO\textsubscript{2} presents a tetragonal structure, with one Ti atom surrounded by six O atoms distributed in a distorted octahedral. In the bulk structure, Ti atoms are six-fold (6f) and oxygen atoms are threefold coordinated. While, on the rutile(110) surface as shown in Figure 1.3, there are two types Ti atoms, five-fold (5f) and 6f coordinated Ti atoms, as well as two-fold (2f) coordinated oxygen atoms (bridging oxygen atoms) and three-fold (3f) coordinated oxygen atoms. On the perfect stoichiometric rutile TiO\textsubscript{2} (110) surface, 5f Ti atom row, 6f atom rows and 3f oxygen atom rows lie in a plane of along the [001] direction, while bridging oxygen atom rows locate above 6f Ti rows in the same direction. The surface of (110) cleaved rutile has been proved to be auto-compensated and charge neutral, as well as breaks the minimum number of bonds and the longest bonds in the crystal structure, which consequently is the lowest-energy surface structure, by means like first-principles calculations and STM.\textsuperscript{[39,40]} For the freshly cleaved surface, the first few layers on the TiO\textsubscript{2} rutile(110) structure will relax to saturate the dangling bonds. As a result, a rumpling structure is created by two different types of Ti (5f Ti and 6f Ti) atoms moving in opposite direction on the top several atomic layers. The unit cell of TiO\textsubscript{2} rutile(110)-(1×1), therefore, is defined as
two adjacent 5f-Ti atoms in [001] direction is with a distance 2.96 Å, and two adjacent 5f-Ti atoms in [1-10] direction with a distance of 6.5 Å.\textsuperscript{41-44}

![Diagram of the crystal structure of TiO₂ rutile(110) surface, with 5f-Ti, O\textsubscript{br} and surface OV marked.\textsuperscript{44}]

Figure 1.3 Diagram of the crystal structure of TiO\textsubscript{2} rutile(110) surface, with 5f-Ti, O\textsubscript{br} and surface OV marked.\textsuperscript{44}

![STM images of TiO₂(110)-(1×1) surfaces with different surface species. (a) a reduced surface with OVs, (b) partially hydroxylated surface with OH groups, and (c) fully hydroxylated surface with OHPs. (d) Height profiles of the labeled sites in (b) for OV, OH, and OHP, respectively. All the STM images have a size of 11 nm × 11 nm, and were obtained at V = 1.6 V, I = 10 pA. \textsuperscript{45} Reprinted with permission from American Chemical Society.]

Figure 1.4 STM images of TiO\textsubscript{2}(110)-(1×1) surfaces with different surface species. (a) a reduced surface with OVs, (b) partially hydroxylated surface with OH groups, and (c) fully hydroxylated surface with OHPs. (d) Height profiles of the labeled sites in (b) for OV, OH, and OHP, respectively. All the STM images have a size of 11 nm × 11 nm, and were obtained at V = 1.6 V, I = 10 pA. \textsuperscript{45} Reprinted with permission from American Chemical Society.
Plenty of STM images have been acquired from TiO$_2$ rutile(110)-(1×1) surface which are consistent with the theoretical structure in Figure 1.3. Most images are obtained on empty-state mode, because normally on filled-state mode the tip will scrape on the surface. Limited images on filled-state mode were achieved by some groups.$^{[46,47]}$ The bright rows along [001] direction are composed of 5f Ti atoms, while the dark rows are assigned to bridging oxygen atoms on empty-state imaging mode. This contrast is dominated by the distribution of density of states despite bridging oxygen atoms are higher than 5f Ti atoms in physical geometry structure.

Figure 1.5 STS measurements on TiO$_2$ rutile(110)-(1×1) surfaces. (a) $dI/dV$ of the occupied state of different site at 78 K: a, at the center of a lobe in the occupied STM image between the two 5f Ti sites indicated in the inset STM image. b, at a 6f Ti site. c, at the OV$_{br}$ site. Insets are the STM image and the $I$-$V$ curves corresponding to the three $dI/dV$ curves.$^{[47]}$ Reproduced with permission from AIP Publishing. (b) STS measured above OV$_{br}$ and above regular 5f/Ti surface atoms on TiO$_2$ rutile(110) surface at 78 K, with the measurement range from -3 V (occupied state) to 1.5 V (empty state).$^{[48]}$ Reproduced with permission from American Physical Society.

Many types of surface defects have been observed on TiO$_2$ rutile(110)-(1×1) surface. Three types of intrinsic point defects in the reduced TiO$_2$ rutile(110), including OV defect marked as I, hydroxyl group (OH group) marked as II and hydroxyl group
pairs (OHP), are shown in Figure 1.4. Normally, in ultra-high vacuum (UHV) OV s are created by the reduction of rutile by heating or ion sputtering, while OH groups are created by the dissociation of water at the oxygen vacancies. Although these defects are all bright by STM and locate at the middle of two adjacent 5f Ti atoms rows, the heights at same scanning conditions by STM are different. For example, as shown in Figure 1.4, the height of OHP (1.6 V, 10 pA) is around 1.2 Å and 1.0 Å for OH at the same scanning conditions. While for OV the height is much less than OH and OHP. It is also found that the relative apparent height of OH groups are sensitive to the tip-sample distance in STM measurements, which were not observed on OV and 5f Ti atoms.[45]

Figure 1.6 (a)-(d) Dynamic processes of the dissociation of water at an OV site on TiO$_2$(110) at about 187 K. Protrusions are labeled as follows: OV, OH$_{br}$ groups and water on 5f Ti sites are marked as open white circles, filled white circles and filled black squares, respectively. (e) Schematic diagram of the dynamic processes of water dissociation on the rutile(110) surface.[50] Reproduced with permission from American Physical Society.
Besides getting the surface morphology with atomic resolution of TiO$_2$, the electronic band structure TiO$_2$ has been studied by STM, which is strongly relevant to its performance in many applications.$^{[45,46,48]}$ As shown in Figure 1.5 (a), Minato et al. use scanning tunneling spectroscopy (STS) to identify the occupied Ti 3$d$ defect state of TiO$_2$. While in the work of Setvin et al. (Figure 1.5 (b)) no clear differences between the LODS of 5$f$ Ti atoms and OV were observed.

Figure 1.7 Two sets, (a)-(b) and (c)-(e) show two reaction processes between O$_a$ and water at 300 K, with the interpretation illustrated by the diagram below.$^{[57]}$ Reproduced with permission from American Physical Society
Since the Fujishima and Honda found the photocatalytic water splitting by TiO$_2$, the study of the interaction of water on TiO$_2$ prospers in last several decades, particularly detailed understandings of water adsorption, diffusion, and dissociation on prototypical TiO$_2$ rutile(110).\[^{49}\] Besides that, the study of the interaction of water with TiO$_2$ surface is inevitable to fully understand the chemical and catalytic properties of TiO$_2$, because water always be present either as part of an aqueous environment or as water vapor, even in UHV conditions.

Many research demonstrate that dissociative adsorption of water happens at OV sites on reduced TiO$_2$ surface, followed by the appearance of OHP located on two neighboring O$_{br}$ sites, with the details of the dissociation of water shown in Figure 1.6.\[^{50}\] The dissociative adsorption of water molecules and the tip assisted dissociation of water molecules and OH have also been reported by many groups.\[^{51-56}\] While on oxide TiO$_2$ surface, not only the dissociative adsorption of a water molecular is observed at an OV site, but also the formation of a new water molecule at 300 K, as revealed in Figure 1.7 by STM.\[^{57}\]

Other TiO$_2$ surfaces have also draw abundant attentions, for examples, rutile(011), (100) and (001), as well as anatase(101) and (001), because the phase and facet are recognized to be closely related to the (photo)catalytic performances.\[^{58,59}\] It is also known that the mixed TiO$_2$ of rutile and anatase even exhibit much better photocatalytic activity than the individual polymorphs, due to the proper band alignment could effectively promote the separation of photoexcited charge carriers.\[^{60,61}\] Among these studies, anatase(101), which is the most frequently exposed surface of this high active TiO$_2$ polymorph, has been widely studied.\[^{35,62-68}\] As shown in Figure 1.8, water monomer appears as isolated black spot surrounded by two bright features (whit-black-white, w-b-w). In addition, through STM it was found that at 190
K, water monomer appearing as w-b-w can hop on the surface, as shown in Figure 1.8 (c)-(f). With more water on the surface (0.24 ML), they tend to form a (2 × 2) superstructure on the surface, induced by the charge rearrangement at the molecule-anatase interface.[62]

Figure 1.8 (a) Schematic diagram of the crystal structure of anatase(101) surface. (b) STM image of anatase(101) surface at empty state, with unit cell marked by the black rectangle containing two equivalent Ti_{5c}/O_{2c} surface atoms, and a water monomer marked by the black arrow. (c) and (d) two consecutive STM images of anatase(101) surface with 0.11 ML water on the surface, showing the hopping of water monomer during STM scanning. (e) Difference image of c and d. (f) Height profiles crossing a water molecule, and two adsorbed water molecules along the blue and red line in d, respectively. (g) Ordered water overlayer in (2 × 2) on anatase(101), as indicate by the red unit cell.[62] Reproduced with permission from Springer Nature.

1.2.3 Semiconductor photocatalyst and photo(electro)catalysts

Photocatalysis, through which one can convert solar energy into chemical energy, has been regarded as one of the most promising strategies to solve crisis of energy shortage and environmental pollution. It has been demonstrated to exhibit great potential in several applications, including photocatalytic water splitting, photosynthesis, and the treatment of pollutants in aqueous or gas phase.[69-72] Unfortunately, reliable photocatalysts are scarce, although the appeal of the direct
conversion of solar into chemical energy via semiconductor compounds has been recognized for a long time. This is mainly due to their low solar-energy conversion efficiency, especially in the visible-light spectrum.

Generally, a typical photocatalytic process involves three steps: (i) absorption of solar light (with the efficiency denoted as $\eta_A$), (ii) separation of photoexcited charge carriers (with the efficiency denoted as $\eta_S$), and (iii) reduction or oxidation reactions at the surface to complete the solar energy conversion (with the efficiency denoted as $\eta_C$). The overall efficiency ($\eta$) is therefore determined by multiplying the efficiencies of the individual steps: $\eta = \eta_A \times \eta_S \times \eta_C$. Thus, several criteria are essential for the design and development of novel photocatalysts that possess high solar-energy conversion efficiency. First of all, the band gaps of the photocatalysts should be narrow enough ($E_g < 3.0$ eV), which allow absorption of both ultraviolet (UV) and visible light in the solar spectrum. This is because UV and visible light account for 5% and 43% of the solar spectrum, respectively. Secondly, a high separation rate and high mobility of the photoexcited charge carriers (electrons and holes) are essential for high-efficiency photocatalysts. The former can lead to high quantum conversion efficiency, while the latter increases the effective charge-carrier diffusion length and thus enhances the photocatalytic activity. For semiconductors, the mobility of electrons and holes is determined by their effective mass ($m^*$). As shown in Equation 1.1, the $m^*$ is estimated to the second order derivative of energy ($E$) with respect to the wave vector ($k$), which is reflected by the curvature of the band edges.

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \times \frac{d^2E}{dk^2} \quad (1.1)$$

As illustrated in Figure 1.9 (a), a larger curvature of the band leads to a small $m^*$ (light effective mass) of the charge carriers. This means the dispersion of the electronic band determines $m^*$, that is, the more dispersive the band the smaller $m^*$ will be, and
consequently, the higher the mobility it will have. In contrast, a dispersion-less band leads to large $m^*$ (heavy effective mass) of charge carriers with low mobility. Thirdly, the positions of the valence and conduction bands (VB and CB) are of importance to determine the chemical potential of photoexcited electrons and holes, which have significant impact on the efficiency of different photocatalytic reactions (Figure 1.9 (b)). The overall solar-energy conversion during the photocatalysis process is, therefore, determined by the electronic structures of photocatalysts.

![Diagram of the relationship between the band shape and the effective mass of electrons and holes. (b) Diagram of the band structure of direct-gap semiconductors, illustrating its role in determining the catalytic properties of photocatalysts.](image)

Surface and interface properties of semiconductors play a vital role in determining their photocatalytic activity. This is not only because nanostructure or microstructure with very large specific surface area are desired, but also due to electronic structure of photocatalysts and separation of photo-excited electron-hole pairs can be effectively tuned through surface and interface engineering.\textsuperscript{[73]}
1.2.4 BiOBr based catalysts

BiOX (X = Cl, Br, I and F) belongs to the family of bismuth oxyhalides (Bi$_x$O$_y$X$_z$). As a heavy metal, bismuth atoms tend to form very weak bonds with non-metal elements, which generally tend to have small molecular orbital overlap and favors the establishment of narrow band gaps. Along with a narrow band gap, a small effective mass may to be acquired for semiconductors with similar crystal and band structures, according to the $k$-$p$ perturbation theory. Various bismuth oxyhalides compounds exhibit high visible-light activity towards photocatalytic degradation of organic and inorganic toxic substances, water splitting, CO$_2$ reduction and N$_2$ fixation.$^{[74-84]}$

Their VB maximum is mainly composed of O 2$p$ and X $n$p states ($n$ = 3, 4, and 5 for Cl, Br, and I, respectively). Their CB minimum in most cases is constructed from Bi 6$p$ states.$^{[85-87]}$ Thus, the band structures of bismuth oxyhalides are expected to be tunable via the halogen species and the ratios of Bi:O:X. Meanwhile, due to the dispersive properties of the $p$ and $s$-$p$ hybridization states, high-mobility charge carriers can be obtained in many bismuth oxyhalides compounds.

As shown in Figure 2.0 (a) and (b), both experimental and theoretical works have suggested that the band gap of BiOX can be gradually narrowed from 3.4 eV for BiOCl to 2.8 eV for BiOBr and 1.9 eV for BiOI, due to the increasing participation of the X $n$p states.$^{[88,89]}$ As a result, Zhang et al. proved that BiOI shows a wider visible-light absorption range than BiOCl and BiOBr, and higher visible-light photocatalytic activity towards degradation of methyl orange (MO)$^{[90]}$. On the other hand, due to the appropriate VB edge, BiOBr and BiOCl exhibited much higher oxygen evolution efficiency and better photocatalytic degradation of Rhodamine B (RhB) and phenol under visible light or simulated sunlight irradiation than BiOI.$^{[88,91]}$ As shown in Figure 2.0 (d) and (e), Bhachu et al. demonstrated that BiOBr also had much superior water
oxidation activity compared to BiOI and BiOCl under simulated sunlight irradiation, due to its more positive VB edge.\textsuperscript{[92]} It should be noted that for Bi\textsubscript{x}O\textsubscript{y}X\textsubscript{z} photocatalysts, the nature of their internal electric field contributes to the efficiency of separating photoexcited charge carriers, which is induced by their layered structure, consisting of interleaving positive [Bi-O] layers and negative X layers.\textsuperscript{[93,94]}

![Image](image-url)

Figure 2.0 (a) Ultraviolet-visible (UV-Vis) diffuse reflectance spectra of BiOX (X = Cl, Br, and I).\textsuperscript{[85]} (b) Calculated band gap and the band alignment of the BiOX (X = Cl, Br, I and F) compounds by density functional theory (DFT).\textsuperscript{[89]} (c) Oxygen evolution of BiOX under simulated sunlight irradiation.\textsuperscript{[29]} (d) Photoanodic activity measurement of BiOBr film under simulated sunlight irradiation. (e) Stability of the BiOBr film at an applied voltage of 1.0 V vs. Ag/AgCl.\textsuperscript{[92]}

Adjusting the ratio of Bi:O:X in bismuth oxyhalides has also been demonstrated to be an effective approach to obtain visible-light photocatalysts with the desired electronic structure.\textsuperscript{[76,77,95,96]} Shang et al. reported that Bi\textsubscript{24}O\textsubscript{31}Br\textsubscript{10} ($E_g \approx 2.8$ eV,
similar to BiOBr) exhibited considerable photocatalytic activity towards Cr(VI) ion reduction and H₂ evolution through water splitting. BiOBr cannot split water to release H₂ through photocatalytic reactions, however, because its conduction band minimum (CBM) is more positive than the electrode potential of H⁺/H₂. While in the case of Bi₁₂O₃₁Br₁₀, the CBM, mainly consisting of hybridized Bi 6p and Br 4s orbitals, is uplifted to be more negative than the electrode potential of H⁺/H₂, which enables Bi₁₂O₃₁Br₁₀ to reduce water into H₂ under visible-light irradiation. In addition, the hybridization s-p orbitals lead to a dispersive band, which is expected to increase its efficiency through promoting the separation of the photoexcited electrons and holes.

Surface engineering has successfully been implemented in promoting the photocatalytic activity of bismuth oxyhalides. Manipulations of exposed facets have been achieved in a variety of BiOX photocatalysts, in which the tunable exposed facets can efficiently adjust their photocatalytic activities. Morphology and thickness engineering are also efficient approaches for modulating the photocatalytic activities of bismuth oxyhalides through adjusting their the exposed surfaces, specific surface area and electronic properties, which are closely relevant to their layered structures.

In addition, OVs have been reported to be particularly efficient in promoting the photocatalytic activity of ultra-thin bismuth oxyhalides nanosheets. For examples, enhanced photocatalytic performances in dye degradation by BiOCl, and CO₂ reduction by BiOBr through introducing OVs in their ultra-thin nanosheets. It demonstrates that effect of defect engineering could be more effective for semiconductor photocatalysts in 2D, which has a very high specific surface area and more sensitive electronic properties compared with bulk materials.
1.3 Outline of chapters

Chapter 2 introduces the experimental instruments used in this thesis. SPM techniques, comprising AFM and STM, are illustrated in details of their working principles and applications. Other facilities, including electron microscopies (SEM, TEM and STEM) and photoelectron spectroscopy (XPS and UPS), which are widely applied in the study of surface science and technology, are also introduced.

Chapter 3 presents STM study of the evolution of the TiO$_2$ rutile(110) surface with increasing oxygen deficiency, which was created by annealing in vacuum condition. At 900 K, the surface exhibit a (1×1) structure with isolated OV point defects. While at 1300 K, the surface changed to (1×2) reconstruction with cross-links defects dominating the surface.

Chapter 4 presents the surface study of OV-TiO$_2$(110) surfaces by STM and STEM. The effect of OVs on the electronic properties were further revealed by photoelectron spectroscopy. More importantly, the vital roles of OVs on the greatly enhanced electrocatalytic activity toward HER were revealed under the combination of surface studies and DFT calculations. The promoted electrical conductivity and hydrogen desorption capability induced by OVs were suggested to be decisive in the enhanced electrocatalytic activities.

Chapter 5 presents the study of modification of inner strain in 2D {001} facets exposed BiOBr nanosheets. The effect of strain on the crystal structure and electronic structure were revealed by TEM and DFT calculations. It is also demonstrated that the photocatalytic performance of BiOBr in dye degradation can be manipulated by the strain effect. The improved charge separation attributable to a highly dispersive band structure in low-strain BiOBr nanosheets contributed to the promoted photocatalytic activities.
Chapter 6 presents the strain induced 2D lateral pseudoheterogeneous structures in 2D BiOBr nanosheets. AFM, TEM and STEM characterizations revealed that the pseudoheterogeneous interface without atomic mismatch can be feasibly modulated by local strain distribution, which exhibits similar local electronic band structure of corresponding heterostructures. Significant enhancement in charge separation at the pseudoheterostructure was demonstrated under visible light irradiation of individual single nanoplates, which is given rise to the controllable electronic band alignment across the interface. The construction of the lateral pseudoheterostructure offers a feasible and promising way to build unprecedented 2D systems with exciting properties.

1.4 References


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Chapter 2 Experimental Techniques

2.1 Scanning tunneling microscopy

STM was firstly demonstrated in 1982 by Gerd Binning and Heinrich Rohrer, who were later awarded the Nobel Prize in physics in 1986 for their design of STM.\textsuperscript{[1,2]} STM can achieve atomic resolution on the conductive surface of semiconductors and metals, and is able to acquire the local density of states (LDOS) as function of position on the surface. In addition, STM has also demonstrate its strong capability of manipulating and transferring atoms on the surface. As a consequence, STM is applied in a wide range of research and application fields, including physical, chemical, biological, material, and nano science and technology.

2.1.1 Quantum tunneling

The quantum tunneling effect is a quantum phenomenon that has no counterpart in classical physics. A particle has a probability to tunnel cross a barrier, even though the energy of the particle is less than the barrier height. These barriers can either be physically impassable medium, including insulators or vacuum, or a region of high potential energy.
Figure 2.1 Quantum mechanical tunneling through a potential barrier of height (V) and width (D).

The quantum tunneling probability of a particle can be determined through solving Schrödinger equation. As shown in Figure 2.1, the incident particle from the left of the energy barrier (width D) has a free particle wavefunction of an energy smaller than the potential barrier of height (V). When the incident particle approaches the barrier, the Schrodinger equation can be described as:

\[-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x)}{\partial x^2} = (E - V) \Psi(x) \] (2.1)

The solution is:

\[\Psi = A e^{-\alpha x} \] (2.2)

where the decay constant \(\alpha\):

\[\alpha = \sqrt{\frac{2m (E-V)}{\hbar^2}} \] (2.3)

Therefore, the decay constant depends not only on the energy barrier but also the mass \((m)\) of the particles and the reduced Planck constant \((\hbar)\).
2.1.2 Working principle of STM

STM is designed based on the principle of quantum tunneling of electrons between a sharp metallic tip and the conductive surface, when they have a close distance within several angstroms. Meanwhile, in order to achieve the scanning of the surface, a 3-dimisonial piezoelectric scanner with the sub-angstrom precision in both x-y plane and z direction are need. When a voltage between the tip and the sample is given, electrons can tunnel between them. For example, if a positive voltage is applied on the sample, electrons will tunnel from the filled state of the tip to the empty states of the sample when they are in the tunneling region, and vice versa. The tunneling current can be calculated using the time-dependent perturbation theory. If a positive V is applied to the sample, the Fermi level of the sample shifts down with respect to the Fermi level of the tip, and electrons tunnel from the occupied states of the tip into the empty states of the sample. The net electric current, which is in the range of picoamperes to nanoamperes, then can be detected. The intensity of the tunneling current is proportional to the overlap between the wavefunctions of tip and sample, which depends strongly on their distance. A typical setup of STM system is illustrated in Figure 2.2.

![Figure 2.2 Diagram of the setup of STM system.](image_url)
The total tunneling current can be estimated by the perturbation theory$^{[3-5]}$:

$$I(V) \propto \int \rho_s(E) \rho_t(E - eV) |M_{ts}(E, V, z)|^2 (f(E - eV, T) - f(E, T)) dE \quad (2.4)$$

where $\rho_s$ is the DOS of sample, $\rho_t$ is the DOS of tip, $E$ is the energy of electrons, $T$ is temperature, $f$ is Fermi function, $V$ is the applied voltage, $M_{ts}(E, V, z)$ is the tunnel matrix.

According to Tersoff-Haman approach, $\rho_s$ and $\rho_t$ can be treated as constant under small bias voltage. Considering in STM studies, low temperature and metallic tips (such as W or PtIr) with flat DOS around Fermi level are applied, the expression for the tunneling current can be simplified as:

$$I(V) \propto \int \rho_s(E) dE \quad (2.5)$$

Therefore, the tunneling current under certain bias $V$ is proportional to the integral of the DOS of the sample from the Fermi level to $eV$.

For the widely adopted constant-current mode, a feedback loop is used to regulate the distance between STM tip and the sample in the z-direction to maintain the set-point current. Then the change of the $z$ position of the tip can be obtained to produce the surface topography.

Meanwhile, tunneling current is dependent on distance between STM tip and sample, and the integral of the DOS from Fermi level to $eV$. For a sample with a homogenous DOS, the topography is entirely contributed by the geometric surface profiles. Whereas, considering that most materials exhibit a spatially inhomogeneous DOS, the obtained STM images are dominated by both the geometric surface profile and the local DOS.

As the measured tunneling current is proportional to the integral of the DOS of the sample from the Fermi level to $eV$, STM can also acquire the local DOS (LDOS) of a
selected energy range on the surface by fixing distance between STM tip and the sample. This means the LDOS can be directly measured by sweeping the applied voltage at a fixed position on the surface, which can be explained by Equation 1.6 (Derived from Equation 2.5). Instead of numerical calculation of the obtained tunneling current and the applied voltage that is easily be affected by the noise, lock-in amplifier technique is widely employed to directly record the $dI/dV$ signal, which works through applying a small bias voltage modulation $dV$ to the applied $V$ and record the change in the tunneling current $dI$.

$$\frac{dI}{dV} \propto \rho_s(eV) \quad (2.6)$$

2.1.3 Ultra-high vacuum system and molecular beam epitaxy

In the LT-STM and MBE combination system, UHV condition is necessary for acquiring highly clean sample surface, and high resolution and stable images. To achieve UHV (less than $1 \times 10^{-10}$ Torr) in our system, a serious of supporting structures and vacuum pumps are used, as illustrated in the setup diagram in Figure 2.3.

![Figure 2.3](image.png)

Figure 2.3 The relative schematic vacuum layout of our STM/MBE system.

A load-lock is designed for loading and transferring samples and STM tips into the UHV preparation chamber without venting the chamber to atmosphere. The vacuum of
Load-lock chamber is achieved by to $10^{-9}$ Torr. Load-lock chamber is separated from preparation chamber and observation chamber by a gate valve (GV). To obtain the a UHV condition for preparation chamber and observation chamber, the system needs to be firstly pumped by a combination of rotary pump and turbo molecular pumps (TMP) to the vacuum level around $1 \times 10^{-9}$ Torr after baking (generally 100 °C to 250 °C). Then under the pumping of ion pump and titanium sublimation pump (TSP), the system can reach an UHV condition of $5 \times 10^{-11}$ Torr.

Figure 2.4 The relative schematic of preparation chamber with MBE system.

Molecular beam epitaxy (MBE) is an advanced UHV epitaxy method with high precision of sub monolayer and purity. The key aspect of MBE is the slow deposition rate, which enable the precisely control of the amount of dopants or thickness of crystal film. In the UHV environment, atom or molecular beams are thermally evaporated and deposit on a heated substrate placed in the line of sight of the beam line, as shown in
the relative schematic of our preparation chamber. The widely adopted evaporation source in commercial MBE is Knudsen Effusion Cell (K-cells), which consists of mechanical shutters, boron nitride or aluminum oxide crucible, tungsten filament heater, tantalum heat shielding, thermocouple, and cooling water system. Other facilities, for examples the heating stage and the argon sputtering gun, are also installed in the preparation chamber for both sample deposition, treatment and cleaning.

2.2 Atomic force microscopy

Atomic force microscopy (AFM), which is another important SPM technique beyond STM, was developed by Gerd Binning et al. in 1986.\textsuperscript{[6,7]} Different with STM which was designed based on the quantum tunneling effect between STM tip and sample surface, AFM works through measuring the force interaction between AFM tip and sample surface. Thus, the application scopes of AFM are not limited for conductive samples, but also can be extended to almost any measurable force interaction, including van der Waals, electrical, chemical bonding, magnetic, thermal, and capillary forces, which enable AFM to be the most versatile SPM technique.\textsuperscript{[8]} Thus, combining the high-resolution for 3D topography, capability of operating in ambient conditions and liquid conditions, and integrating with variety of optical microscopy and spectroscopy techniques, AFM has been widely employed in measuring surface topography and detecting force interaction in many research fields, such as material science, condensed matter physics, nanoscience and nanotechnology, chemistry, biology, and medicine.

2.2.1 Working principles of AFM

AFM, typically, mainly consists of a sharp tip fixed on a cantilever, laser beam and optical system, laser detector and feedback system, display and processing system, and piezo-based scanning stage, as shown in Figure 2.5.
$F_{ts} = -\frac{\partial V_{ts}}{\partial z}$ (2.7)

where $F_{ts}$ is the tip-sample force and $V_{ts}$ is the potential.

When a sharp AFM tip approaches close a sample surface, a force will arise between AFM tip and the sample due to the potential energy, which is illustrated in Equation 2.7. Then the force lead to a deflection of the cantilever according to Hooke's law, with the spring constant $k_{ts}$ determined as:

$k_{ts} = -\frac{\partial F_{ts}}{\partial z}$ (2.8)

$F_{ts}$ can be divided into long-range and short-range forces. For the ambient AFM system employed in this thesis, long-range force typically represents the attractive forces, including Van der Waals force, magnetic force, capillary force, and electrostatic force. While, short-range force can be measured in vacuum conditions when the tip-sample distance can reach less than several angstroms), chemical force, covalent force, electrostatic, magnetic and Van der Waals forces can be determined.

2.2.2 Working modes of AFM

There are basically three operation modes of AFM classified by the way of tip motion, including contact mode, tapping mode and non-contact mode. These different
working modes can be adopted in different interaction forces, and corresponding applications. Figure 2.6 illustrates the relationships between AFM working modes and the force ranges. Normally, contact mode and tapping mode are used in ambient environment, while non-contact mode is mostly used in vacuum. Therefore, only contact mode and tapping mode are introduced in this thesis.

![Typical Van der Waals force curve](image)

Figure 2.6 Classification of AFM working modes based on Van der Walls force curve.

**Contact mode-AFM**

In contact mode, the AFM tip directly contact with the sample surface under repulsive force. The constant force mode is mostly adopted for most applications. During the scanning, the deflection of the cantilever is kept constant, which enables the force to be constant. The constant deflection of the cantilever is controlled by an active feedback loop that can adjust the tip and sample surface distance corresponding to the topography. For constant height mode, the spatial variation of the cantilever deflection, in contrast, is directly recorded to yield the topography of sample surface. Constant
height mode is mostly employed only for acquiring atomic resolution of sample surface. In addition, based on contact mode AFM, a series of functions have been developed, for examples, force spectroscopy and mapping, lithography and nanomanipulation, conductive AFM, and so on.

**Tapping mode-AFM**

In tapping mode, the AFM tip oscillates above sample surface under a driving frequency very close to the resonance frequency of the cantilever. During the scanning, the oscillation amplitude of the cantilever is kept constant through the feedback loop, when the tip periodically contacts with sample surface. As the force between the tip and sample surface changes, the feedback loop will adjust the height to maintain the set oscillation amplitude of the cantilever, which reflects the force distribution or the topography of the sample surface. In tapping mode, as the tip gently interact with sample surface, both the tip and sample are less destructive compared with contact mode. In addition, in tapping mode, the phase lag of the cantilever oscillation relative to the signal sent to the driving piezo can be simultaneously recorded. The phase channel reflects the energy dissipated by the cantilever during the scanning, which can reveal the stiffness or adhesion information of sample surface.

**Kelvin probe force microscopy (KPFM) combined with Tapping mode**

KPFM, also known as surface potential imaging, has been well developed combined with tapping mode AFM, in which the difference between the potential of the tip and that of the sample can be determined.\[9,10\] The data obtained in this mode is a combination of three contributing factors: the work function difference, trapped charge, and any permanent or applied voltage between the tip and the sample. As a consequent,
KPFM is generally considered a pseudo-quantitative technique, in which the acquired accurate contact potential difference (CPD) mostly consists of more than one physical quantity. In KPFM measurement, an AC bias ($V_{AC}$) is usually applied on a conductive tip to oscillate the electrostatic force between tip and sample. The feedback loop then can provide a DC bias ($V_{DC}$) to the tip to minimize the electrostatic force between the tip and the sample.

The electrostatic force between the tip and the sample under the $V_{AC}$ can be described as Equation 2.9, when they are modeled as a parallel plate capacitor.

$$F = \frac{1}{2} \frac{\partial C}{\partial z} V^2 \quad (2.9)$$

The total potential difference ($V$) between the tip and the sample is the sum of $V_{AC}$, $V_{CPD}$, and the $V_{DC}$, as shown in Equation 2.10.

$$V = V_{CPD} + V_{DC} + V_{AC}\sin(\omega t) \quad (2.10)$$

Therefore, the electrostatic force can be described as:

$$F = \frac{1}{2} \frac{\partial C}{\partial z} \left( [(V_{DC} - V_{CPD})^2 + \frac{1}{2} V_{AC}^2] + 2[(V_{DC} - V_{CPD})V_{AC}\sin(\omega t)] - \frac{1}{2} V_{AC}^2\cos(2\omega t) \right) \quad (2.11)$$

The first part represents force is static and not frequency dependent. The second part occurs at the drive frequency $\omega$. The third part reacts at twice the drive frequency. As a result, the most important term here as far as surface potential is concerned is the second, since this depends not on the square of the voltage, but rather on the potential difference between the tip and the sample, multiplied by the magnitude of the applied $V_{AC}$. This means that if there is a $V_{CPD}$ between the tip and the sample, then when an $V_{AC}$ voltage is applied, there will be an oscillatory force at the frequency of the drive and proportional of the magnitude of the applied voltage, and also proportional to the CPD. Further, if we make $V_{DC} = V_{CPD}$, with a potential feedback loop between the tip.

42
and the sample, then the oscillations at \( \omega \) will be nulled. Therefore, the CPD can be recorded during the scanning.

2.3 Other facilities

Besides STM and AFM, which can directly probe the surface morphology, and in some extent, visit the surface electronic states and catalytic reactions, other facilities have also demonstrated their capabilities in this research filed. Here, several facilities of electron microscopies, X-ray and electron spectroscopies involved in this work are briefly introduced.

2.3.1 Scanning electron microscopy and focused ion beam

Scanning electron microscopy (SEM) is a very useful and robust facility for imaging the surface morphology of samples with a resolution higher than 1 nanometer, which belongs to the family of the electron microscopes. It works through scanning the electrically conductive sample surface with a focused electron beam. For samples that are not conducting, coating with very thin noble metal film (Au or Pt) enable their surface morphologies to be imaged by SEM. During the interactions between the focused electron beam and sample surface, main products are secondary electrons, backscattered electrons, auger electrons, and characteristic x-rays. These products can be collected by different detectors, which contribute the SEM images. For examples, secondary electrons come from the inelastic interactions between the primary electron beam and the sample, which mostly contributed by the atoms in top surface and near surface regions. It is the most common used SEM mode in imaging the surface morphology. The characteristic x-rays signal can be collected for the energy-dispersive x-ray spectroscopy (EDX), which enables elemental analysis or chemical characterization of sample surface.
Besides SEM, focused ion beam (FIB) is another important technique in the fields of materials science and industry. Different from SEM which is designed based on focused electron beam, FIB commonly uses a focused ion beam, or integrate focused electron beam together. Therefore, FIB is widely used for lithography and etching in micro or nano-scale by the focused high energy ion beam (Gallium ion is most widely used ion source). In addition, FIB has also been used in locally depositing films, modifying and fabricating materials, and preparing transmission electron microscopy (TEM) specimen.

2.3.2 Transmission electron microscopy

TEM is another very important electron microscopy, which is well known as its capability of imaging real-space atomic-resolution of nanostructures. TEM uses high energy focused electron beam to transmit through and interact with the specimen as it passes through it to image the structure, shape, morphology, size and composition of the specimen. The specimen used in TEM are required to be have a thickness less than 100 nm or in nanostructures that can be suspension on a grid, which guarantee effective transmission of electron beam. TEM appears in three different forms of high-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM) and analytical electron microscope (AEM).[11]

The working principle of TEM can be described using a single lens microscope, with the difference in using electrons rather than photons as the source. Figure 2.7 shows the simplified model, in which only the objective lens that determining the resolution are included and the intermediate lenses and projection lenses are omitted. The resolution of TEM can be estimated by the Abbe’s equation modified by the by using DeBroglie’s formula.
\[ d = \frac{0.753}{\alpha V^2} \] (2.12)

where \( d \) is the resolution in nanometer, \( \alpha \) is the half aperture angle, \( V \) is the accelerating velocity of the electron beam. For a TEM system with accelerating voltage of 100 kV, the resolution \( d \) is valued to be 0.24 nm.

![The simplified model of a one-lens TEM based on the Abbe’s theory.][1]

HRTEM is one of the most well-developed tools to in material science with its atomic resolution capability. HRTEM uses both the scattered and transmitted electrons, which is an interference pattern between the forward-scattered and diffracted electron

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[1]: Figure 2.7 The simplified model of a one-lens TEM based on the Abbe’s theory.\textsuperscript{[12]}
waves from the specimen. Therefore, it is a phase contrast imaging mode, which can achieve a resolution as high as 0.1 nm. The acquired diffraction pattern with the information of the specimen, then can be converted to the Fourier transform analysis.

In recent years, STEM has experienced revolutionary development due to the aberration correction technique. Sub-angstrom resolution has been achieved in STEM,[13] which greatly benefits many research filed, such as the solid state physics, materials sciences, catalysis and chemistry sciences. In addition, the successfully implementation of combining high angle annular dark-field (HAADF) mode and electron energy loss spectroscopy (EELS) which belongs to AEM have been achieved. This provides a very powerful approach to coupling high resolution images with the local electronic structure of the specimen, which are valuable for revealing fundamental mechanism for many scientific challenges, especially in the field involving surface and interface.

Different with HRTEM, STEM uses the focused electron to scan over the specimen. The electron beam is focused with the assistance of the aberration correction to reach a fine spot in the order of sub-angstrom. The scattered electrons undergone different interactions are then collected by the different detectors. The most common detectors in commercial STEM include HAADF, annular dark-field (ADF), bright-field (BF), EELS and EDX. The HAADF detector is, in particular, important in acquiring atomic resolution images. It collects the electrons scattered out to high angles, in which electrons are not Bragg scattered. As a result, HAADF images show little or no diffraction effects. The detected intensity of the incoherently scattered electron is highly sensitive with the atomic number and the image contrast has a proportional relationship $Z^2$ according to Rutherford scattering model. Therefore, the extremely high
atomic resolution is determined by the size of the focused electron spot, rather than HRTEM which depended on electron diffractions.

2.3.3 Photoelectron spectroscopy

Photoelectron spectroscopy is the most widely used quantitative spectroscopic technique in analyzing the surface chemical and elemental state, and electronic structure of materials. Photoelectron spectroscopy is designed based on the photoelectric effect, using photo-ionization and measuring the kinetic energy distribution of the emitted photoelectrons. The recorded photoelectron spectrum then can be converted to the binding energy of electrons which represents the energy difference between the ionized and neutral atoms. The relationship is described by the Einstein relationship:

\[ E_b = h\nu - E_k - \phi \] (2.13)

where \( E_b \) is the electron binding energy, \( h\nu \) is the photon energy of the radiation source, \( E_k \) is the kinetic energy of photoelectron, \( \phi \) is the work function induced by the analyzer, which dependent on both the analyzer and the material. This equation is essentially a conservation of energy equation. The work function, \( \phi \), usually can be regarded as constant in the measurement.

According to the different exciting radiation source, photoelectron spectroscopy can be divided into x-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS). As shown in the diagram in Figure 2.8, XPS normally uses soft x-rays (200-2000 eV) as the radiation source and can examine the core-level electrons with a penetration depth of 1-10 nm. While UPS applies vacuum UV radiation (10-45 eV) to examine valence elections of samples with a penetration depth even smaller than XPS due to its lower incident photon energies.
Figure 2.8 Schematic diagram of the electron excitation progress of XPS and UPS.

It has to be mentioned that, the implementation of synchrotron radiation as the excitation source for photoelectron spectroscopy has greatly broaden its applications.$^{[14,15]}$ Compared with the normal x-ray generator, and He lamp for UV light, synchrotron radiation has advantages of high intensity, very broad and continuous spectral range, high flux and brightness, and high degree of polarization, which has been playing a very important role in many advanced research fields, including materials science, physical, biological and chemical sciences, geosciences, environmental sciences, and medical and pharmaceutical sciences.
2.4 References


Chapter 3 Characterization of TiO$_2$(110) surface by STM

3.1 Introduction

TiO$_2$, as a typical TMO, have been widely applied in the field of energy conversion, surface pigments, and photocatalytic wastewater and hazardous gas remediation, due to its catalytic activity and semiconducting properties as well as its earth abundance, low toxicity, chemical and thermal stability.$^{[1-2]}$ Surface and interface engineering has been recognized as an effective approach in promoting the performances or tuning reactivity of TiO$_2$ in catalysis or energy conversion, for examples facet engineering,$^{[3,4]}$ curved surfaces,$^{[5]}$ surface defects,$^{[6-8]}$ surface adsorbates and constructing interface heterostructures.$^{[9-14]}$

Among these strategies, OV is regarded as one of the most important and prevalent defects in TiO$_2$, as well as a large number of metal oxides, which has been widely investigated both by theoretical calculations and experimental characterizations.$^{[15-20]}$ Compared with defects created by doping, OV is the kinds of defect which do not disturb the intrinsic crystal structure and involve other impurity elements. At the same time, OV is thought could contribute excess electrons that will occupy 3d orbitals of the neighboring Ti atoms and forms Ti$^{3+}$ ion, which could enhance the electronic conductivity of TiO$_2$. As a result, OV is expected to significantly affect the physical, chemical and catalytic properties of TiO$_2$, for examples, absorbing and desorbing behaviors toward molecules, electron transfer in the catalyst and between the surface of catalyst and adsorbed molecules, as well as the ability of light absorption.

Therefore, acquiring the detailed knowledges of OV about their location, distribution, as well as effect on electronic structure and adsorption/desorption of
molecules, especially on the surface region, are of great importance toward rationally promote the activity of TiO$_2$ and other TMOs in their applications in catalysis and energy conversions. In this chapter, thermally created OV based defects were introduced into (110) single crystal in vacuum conditions. By carefully controlling the annealing temperature and time, the defect species and concentration on the surface were examined by in-situ STM observations. It was found that at the surface of rutile(110) experienced a reconstruction evolution from (1×1) with point OV defect to (1×2) with cross-links defects, with the rutile(110) single crystal heated from 900 K to 1300 K.

3.2 Experimental section

TiO$_2$ rutile(110) single crystal (5 × 5 × 1 mm) was purchased from Mateck, GmbH. To obtain the reduced TiO$_2$, the rutile single crystals were annealed in UHV at 900 K to 1300 K. The concentration of OVs in the single crystal were controlled by the annealing time and annealing temperature. STM images were acquired by using a low-temperature STM (LT-STM) (USM 1500-M, Unisoku Co.) at 78 K. STM images can be obtained in both constant current mode and constant height mode. Here, STM images were acquired in constant current mode unless noted otherwise. The samples in STM measurements were treated by several cycles of Ar$^+$ sputtering (1 kV, 20 min) and annealing.
3.3 Results and discussion

3.3.1 Rutile(110) surface with (1×1) reconstruction

Figure 3.1 Large scale STM image of the reduced TiO$_2$ surface (1.3 V, 30 pA).

Figure 3.1 shows the large scale STM image of the rutile(110) surface after several sputtering and annealing at 900 K, in which flat terraces were observed. When we zoomed in to the very small scale shown in the empty-state images in Figure 3.2, atomic resolution STM of the surface were acquired in both constant current mode and constant height mode. As the empty-state of TiO$_2$ is dominated by the Ti-$3d$ electronic states, $5f$ Ti atoms and O$_{br}$ atoms appear as bright and dark rows in the empty-state STM image, respectively, which is reverse-contrast of their real topographies. The
lattice constant of was measured to be 0.63 nm by 0.28 nm, with each bright spot representing one 5f Ti atom, which agrees well with the crystal structure in Figure 1.3.

Figure 3.2 Atomic resolution of the stoichiometric rutile(110) surface. (a) constant current mode, 0.5 V, 100 pA, scan size is 6 nm × 6 nm, (b) constant height mode, 0.5 V, 100 pA, scan size is 6 nm × 6 nm.

3.3.2 OV point defects on (1×1) surface

Figure 3.3 The reduced rutile(110) surface with OVs on the surface, 1.2 V, 20 pA.
In the STM image of reduced (sputtered and annealed at 900 K) rutile(110) surface, bright protrusions between two 5f Ti rows can be observed, as indicated by the arrows in Figure 3.3. The OVs trends to individually locate between 5f Ti rows. While as the surface stored in the UHV chamber for several hours, other two kinds of bright protrusions appeared on the surface, as shown in Figure 3.4 (a). These three types of bright protrusions (marked as I, II, and III) exhibit different brightness and apparent heights (indicated in Figure 3.4 (b)), which can be used not only in identifying different species, but also in monitoring their dynamic reaction processes.\[21\textsuperscript{-}23\]

Figure 3.4 (a) STM image of the surface of rutile(110) obtained several hours after annealed in the UHV (10 nm × 10 nm, 1.6 V, 30 pA). (b) Apparent height profiles of OV, OH group and H\(_2\)O in STM images. OV, OH, and H\(_2\)O are bright protrusions between two adjacent Ti rows.

They can also be identified by their different responses toward voltage bias plus, which a voltage higher than a threshold voltage (around 2.0 V in our measurements), either through giving pulses or scanning, was applied. As shown in Figure 3.5, when three 2.5 V pulses were applied at the selected OHs marked in Figure 3.5 (a), the hydrogen atoms were removed, allowing the OV to be healed. In the case of OVs, they are always inactive towards 2.5 V pulses or scanning. Therefore, by a combination of their apparent heights and their different behavior under a bias higher the threshold
voltage, we can identify them. This phenomenon indicates that OVs on the surface of rutile(110) are reactive toward water molecules even in UHV conditions and favorable to be hydroxylated on the surface.

Figure 3.5 (a) STM image of the reduced rutile(110) surface with OVs and OHs, 1.3 V, 30 pA. (b) STM image in a same area in (a), in which 2.5 V pulses were applied at the marked OHs, 1.3 V, 30 pA.

3.3.3 Rutile(110) surface with (1 × 2) reconstruction

Figure 3.6 Large scale STM image of the reduced TiO$_2$ surface acquired after annealed at 1300 K, 3 V, 50 pA, with the inset showing the side view of (1 × 2) reconstruction surface.
When the annealed temperature was increased to 1300 K, the flat terraces on (1 × 1) surface evolved to chain structures along Ti rows, as presented in Figure 3.6. This surface has been explained by the (1 × 2) reconstruction due to the more oxygen deficiency at higher annealing temperature.[24-26] In addition some short chains perpendicular to the (1 × 2) chains can be observed, which are marked by the white solid line as links in Figure 3.6. As shown in the zoomed-in images in Figure 3.7, the unit cell of (1 × 2) reconstruction is marked by the black rectangle. Two cross-links of single-link and double-link structure are indicated by the yellow and white arrows. Meanwhile, it notices that the high quality STM image in filled state can be obtained on (1 × 2) surface, which is not applicable on (1 × 1) surface, as shown in Figure 3.7 (b). It indicates that the electronic structures of rutile(110) also undergo significant change with the increasing oxygen deficiency.

Figure 3.7 STM images of rutile(1 × 2) surface. (a) empty state mode, scan size is 10 nm × 10 nm, 1 V, 50 pA, (b) filled state mode, scan size is 10 nm× 10 nm, -1.8 V, 50 pA.
3.4 Summary

OV based defects were introduced into (110) single crystal through annealling in vacuum conditions. By carefully controlling the annealing temperature and time, the defect species and concentration on the surface were examined by in-situ STM observations. On the rutile(110) (1×1) surfaces obtained at 900 K, isolated OV point defects were found, which could be occupied by water molecule or convert to OH. On the (1×2) surfaces obtained at 1300 K, cross-links defects dominated the surfaces.

3.5 References


Chapter 4 Activating titania for electrocatalysis by surface vacancy engineering

4.1 Introduction

As an alternative to fossil fuels, hydrogen is regarded as one of the most promising key energy carriers for a global-scale sustainable energy system.\textsuperscript{[1]} In particular, water-alkali electrolyzers for overall water splitting exhibit tremendous potential for the evolution of high-purity hydrogen and oxygen gases, with the additional values of simple processes, zero CO\textsubscript{2} emission and low pollutant. Finding efficient and low-cost noble-metal-free electrocatalysts towards HER and OER is urgently required for their large-scale commercial application.\textsuperscript{[2-6]} Thanks to extensive efforts, earth-abundant transition TMOs have recently been reported to be promising candidates for electrochemical water splitting in alkaline conditions through defect engineering.\textsuperscript{[7-11]} These defects are expected to effectively improve the intrinsic electrical conductivity of defective TMOs, act as catalytic active cites and enhance the catalytic activity.

Among various defects, surface OV is regarded as one of the most important, and supposed to be the prevalent defect in many TMOs.\textsuperscript{[12-15]} Previous studies have demonstrated that when oxygen atoms are removed from the TMOs, the geometric, physical and chemical properties can be profoundly modified. For example, the coexistence of different oxidation states of metals, such as Ti\textsuperscript{3+}-Ti\textsuperscript{4+} in TiO\textsubscript{2}, Co\textsuperscript{2+}-Co\textsuperscript{3+} in Co\textsubscript{2}O\textsubscript{3} and Ce\textsuperscript{3+}-Ce\textsuperscript{4+} in CeO\textsubscript{2}, are essential in the electron translocations and extremely important for many of their catalytic applications.\textsuperscript{[9,15,16]} Additionally, the surface OV has been well-recognized as favorable adsorption for adsorbates (such as H\textsubscript{2}O, O\textsubscript{2}, metal nanocluster, CO\textsubscript{2}, etc) for the defective TMOs in catalytic processes.\textsuperscript{[17-22]} Obviously, elucidating the role of OV, as well as other defects, in the modified electrocatalytic properties of defective TMOs is of immense scientific and technological importance towards an in-depth understanding and optimizing catalysts.
However, it remains challenging owing to the lack of detailed knowledges of catalytic active sites and the electron translocations at the atomic level. Meanwhile, the precise control of defects is very difficult, because complicated defect compositions along with a wide diversity of sample conditions, such as morphology, crystallinity, dimension and diameters are common in defective TMOs.

Here, in this paper, surface OVs were introduced into the highly pure and stoichiometric TiO$_2$ rutile(110) single crystal, which is a prototypical and widely studied TMO, through thermal treatment under UHV condition.$^{[23,24]}$ STEM and STM techniques found that the as-treated single crystal kept a good crystalline structure. In addition, OVs were found mainly exist in the surface and subsurface region with a depth of around 100 nm rather than the inner bulk region. The simple sample conditions allow us to have an in-depth visit on the effect of OV on the physical and chemical properties of TiO$_2$, as well as its roles in surface electrocatalytic processes. In-situ synchrotron XPS confirmed the appearance of mid-gap defect state in the as-treated single crystal, which was aroused by the associating Ti$^{3+}$ ions with OVs. The catalytic activities of TiO$_2$ were investigated by electrochemical HER in alkaline conditions, suggesting a tremendous enhancement for the as-treated single crystal with OVs. Further STM and DFT calculations suggested Ti$^{3+}$ ions neighboring at OV could be helpful for the proton reduction process and promote the electrons translocation. Gibbs free energy calculations verified that the existence of OV on the surface or subsurface could effectively low the energy of hydrogen adsorption and benefit the HER.

4.2 Experimental sections

The cross-sectional TEM images were acquired with a STEM (JEOL JEM-ARM200f) both in HAADF mode and annular bright-field (ABF) mode. In-situ EELS
was used to characterize the OV concentration of the cross-sectional sample in TEM measurements. The cross-sectional sample was prepared by the FIB (Zeiss Auriga FIB-SEM) technique.

In-situ XPS characterizations were carried out at Beamline 4B9B in the Beijing Synchrotron Radiation Facility (BSRF), and variable photon energies were referenced to a fresh Au polycrystalline film. The spot size of incident light in XPS was about 1 mm in diameter. All the data were recorded in UHV at room temperature. The Hall coefficient and magnetoresistance were measured by the five-probe technique using a Quantum Design Physical Property Measurement System (PPMS)-14T. The electrolyte was 1 M KOH solution. The electrochemical HER experiments were performed by a typical three-electrode method, in which a Pt plate and Hg/HgO (0.923 V versus the standard hydrogen electrode) were used as the counter and reference electrodes, respectively. All electrochemical measurements were performed with a Bio Logic Science Instruments VSP-300 electrochemistry workstation. The linear portions of Tafel plots were fitted to the Tafel equation: \( \eta = b \log|J| + a \), where \( \eta \) is the overpotential, \( a \) is the exchange current density, and \( b \) is the Tafel slope.

All DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP). The generalized gradient approximation (GGA) was applied to treat the exchange correlation energy with the Perdew-Burke-Ernzerhof (PBE) functional. The projector augmented wave (PAW) method was employed to describe electron–ion interactions, with the cut-off energy of 400 eV. The structural model of the TiO_2(110) surface was constructed with four Ti-O layers as a 4 \( \times \) 2 periodic supercell comprising 192 atoms with a vacuum spacing of 20 Å to avoid interaction between adjacent surfaces. Spin-polarized local density approximation plus on-site Coulomb self-interaction potential (LDA+U) calculations were performed for the Hubbard
correction, and an effective U (U_{eff}) value of 4.2 eV was applied in all calculations. All structures in the calculations were relaxed until the convergence tolerance of the force on each atom was smaller than 0.02 eV. The energy convergence criterion was set to be $1 \times 10^{-4}$ eV for self-consistent calculations, and $k$-point sampling was restricted to the Gamma point only because of the large size of the supercell.

4.3 Characterization of OV by STEM

![Diagram of Crystal structure mode](image)

Figure 4.1 Crystal structure mode of the TiO$_2$ rutile(110) surface, surf-OV can be created through removing O$_{br}$ atoms.

![SEM image](image)

Figure 4.2 SEM image of reduced TiO$_2$ single crystal sample cut by a focused ion beam (FIB); inset is an enlarged image of the selected area.
First of all, pure and stoichiometric TiO$_2$(110) single crystal can be well described by the structure model shown in Figure 4.1, with alternating rows of bridging oxygen (O$_{br}$) atoms and five-coordinate titanium (Ti$_{5c}$) atoms lying in a plane along the [001] direction. The reduced single crystal was obtained through annealing in UHV conditions with base pressures in the low $1 \times 10^{-10}$ torr regime at 900 K. The cross-section of the reduced TiO$_2$ single crystal was characterized by STEM, with the sample prepared by FIB shown in Figure 4.2. The top surface, near-surface and inner bulk region all exhibited high crystallinity, shown in Figure 4.3 (a) and (b), indicating that the formation of OV$_s$ did not interrupt its well-crystalline structure of the reduced TiO$_2$. It should be emphasized that the good crystallinity of the surface area of the reduced sample could exclude the existence of disorder or amorphous surface layer and foreign atoms, which are widely studied in many other cases.$^{[25-27]}$ Moreover, the gradually darkening contrast from inner region to top surface with a thickness of around 80 nm in the STEM image implied the increasing oxygen deficiency and the displacement of Ti atoms, because the contrast is proportional to the average atomic number of atomic columns in HAADF mode.$^{[28]}$
Figure 4.3 Cross-sectional TEM image of reduced TiO$_2$(110) single crystal in ABF, showing a high crystalline structure both in the surface and bulk regions. (b) Large-region cross-sectional STEM image of reduced TiO$_2$(110) single crystal in HAADF mode, in which three areas with different depth from the surface (10 nm, 50 nm, and 100 nm) are marked. (c) and (d) Corresponding in-situ EELS Ti-$L$ edge and low-level spectra of the three regions marked in (b).

To further reveal the effect of OVs on the reduced TiO$_2$ single crystal, in-situ EELS were acquired followed the STEM measurement at three different regions (10 nm, 50 nm and 100 nm from top the surface, marked in Figure 4.3 (b). In the Ti-$L$ edge EELS spectra, the intensity ratio of $d_{z^2}/d_{x^2-y^2}$ which is sensitive towards the Ti-O bonding lengths$^{[29]}$ in the top surface region apparently increased compared with those in the inner regions, agreeing well with the OV induced lattice distortions recognized in above experiments. As shown in the low-level spectrum in Figure 4.3 (d), the three
peaks (6.4 eV, 11.3 eV and 14.6 eV), originating from O 2p orbitals to Ti 3d orbitals, are marked in the region A. Compared with inner region, the peaks at the top surface region (10 nm) exhibited obvious broadening, which were caused by the OV induced lattice distortion and indicated a higher OV concentration near the top surface area.\textsuperscript{[30]} Meanwhile, the peaks at 25.2 eV (peak B) and 48.5 eV (peak C) in the inner region shifted towards lower energy to 24.6 eV and 48.2 eV in the top surface region, due to the emerging of more OVs. Peak B was assigned to transitions between O 2p state and Ti 4sp states. Peak C was assigned to excitations from the Ti 3p core level to 3d excited states.\textsuperscript{[31]} Therefore, the existences of OVs are expected to modify the valence state of their surrounding Ti atoms.

4.4 Characterization the electronic structure by in-situ synchrotron XPS and UPS

To investigate the effect of OV on the electronic structure of reduced TiO\textsubscript{2} single crystal, in-situ synchrotron XPS spectra and valance band spectra, was carried out. As shown in Figure 4.4 (a), after annealing the stoichiometric pure single crystal at 900 K in HUV for 5 h, a broad peak at around 457 eV belongs to Ti\textsuperscript{3+} ions appeared in the Ti 2p XPS spectra.\textsuperscript{[32]} It means the excess electrons from the removed oxygen atoms were trapped by Ti atoms and formed Ti\textsuperscript{3+} ions. In the valence band (VB) spectra shown in Figure 4.4 (b), a peak, locating about 0.8 eV below the Fermi Level appeared after annealing, which is known as the Ti 3d defect state. Meanwhile, a broad peak locating at 12 eV can be seen below the Fermi Level for both samples, which can be assigned to the OHs.\textsuperscript{[33]} The broad peaks reflected the dissociation of water at the surface, which is consistent with the STM observation.
Figure 4.4 (a) In-situ Ti 2p XPS spectra of the pristine and OV-TiO₂ single crystal. (b) VB spectra of pristine and OV-TiO₂ single crystal.

Figure 4.5 DFT calculations of the mid-gap states caused by OVs in TiO₂(110). (a) Calculation of the excess electron distribution of the reduced TiO₂(110) surface with an OV on the top surface. (b) The calculated band structure (left) and DOS (right) of the TiO₂(110) with a surface OV.

In addition, DFT calculation was used to verify the OV-induced changes of electronic structure in the reduced TiO₂. As shown in Figure 4.5, after introducing an OV on the surface of TiO₂(110), the two excess electrons belonged to the removed oxygen atom will bond with two neighboring Ti atoms and form Ti³⁺ ions. The other two cases, including OVs at inner region and surface OHs from water dissociation at
surface OV sites were also included in the DFT calculations, which demonstrated that they exhibited similar results of creating Ti$^{3+}$ ions (Figure 4.6). As a sequence, defect states in the gap, can be observed in the calculated band structure and DOS, which are mainly contributed to the Ti 3$d$ orbitals. Above XPS and DFT results indicate that the band gap Ti 3$d$ defect states originate from these intrinsic defects and associating Ti$^{3+}$ ions in the reduced TiO$_2$.

Figure 4.6 Calculation of the excess electron distribution on the TiO$_2$(110) surface with an OV on the sublayer and with two surface Ad-H. (a) and (b) The calculated band structure and DOS of TiO$_2$(110) with sublayer OVs, respectively. (c) and (d) The calculated band structure and DOS of TiO$_2$(110) with surface Ad-Hs, respectively.
4.5 Electrochemical HER activity of OV-TiO$_2$

Figure 4.7 (a) LSV data on different electrocatalysts for the HER at the rate of 10 mV·s$^{-1}$, inset shows the pristine TiO$_2$(110) single crystal (P), OV-low TiO$_2$(110) single crystal (L), OV-high TiO$_2$(110) single crystal (H), and the Nb-doped TiO$_2$(110) single crystal (Nb). The OV-high TiO$_2$ was tested for 1000 cycles with the LVS curve shown as the red solid and green dashed lines for before and after cycling, respectively. (b) Cycling stability over 18 h of the OV-high sample at a potential of −0.7 V. (c) Tafel plot of the OV-high TiO$_2$. (d) $C_{dl}$ determined from the linear fitting of the capacitive current vs. scan rate, measured from the cyclic voltammetry (CV) curves of OV-high TiO$_2$, OV-low TiO$_2$ and Nb-doped TiO$_2$.

To evaluate the electrochemical HER activity of the reduced TiO$_2$ single crystal, two reduced TiO$_2$ single crystal annealed in HUV at 900 K for 5 h (OV-low) and 50 h (OV-high), and a reference sample (Nb-doped (0.43 at%)) single crystal were selected. The electrochemical behavior for the HER of these samples were then tested at 1 M KOH aqueous solution with a scan rate of 10 mV/s. As shown in Figure 4.7, OV-high TiO$_2$
exhibited considerable HER activity with a current density of 22.8 mA.cm\(^{-2}\) at -0.80 V, while Nb-doped TiO\(_2\) exhibited very weak activity and OV-low TiO\(_2\) was almost not active under the same experimental conditions (IR compensation based on resistance test was applied for all linear sweep voltammetric (LSV) curves, Figure 4.8). Long-term stability of the OV-high TiO\(_2\) was demonstrated by the cycling test of 1000 times (red dash line in Figure 4.7 (a)), and a continuous test at a potential of −0.7 V for more than 18 h (Figure 4.7 (b)).

The linear portions of Tafel plots were fitted to the Tafel equation: \(\eta = b \log|J| + a\), where \(\eta\) is the overpotential, \(a\) is the exchange current density, and \(b\) is the Tafel slope. The Tafel slope of OV-high TiO\(_2\) near the substantial cathodic current region from the HER was plotted to be 187.5 mV.dec\(^{-1}\), as shown in Figure 4.7 (c), which represents the hydrogen generation rate with the applied overpotential. Figure 4.7 (d) shows the double layer capacitance (C\(_{dl}\)) of the three samples, which were valued by fitting the slope of the capacitive current vs. scan rate measured from the cyclic voltammetry (CV) curves (Figure 4.9). The C\(_{dl}\) value has a proportional relationship with the electrochemically active surface area (EASA) of catalysts. Therefore, the C\(_{dl}\) value of OV-high TiO\(_2\) at 72 mF.cm\(^{-2}\) demonstrated an apparent increase in the EASA compared with Nb-doped TiO\(_2\) with a C\(_{dl}\) value of 8.8 mF.cm\(^{-2}\), which match well with their HER performances. It should also be noticed that despite the C\(_{dl}\) value of OV-low (16.0 mF.cm\(^{-2}\)) is higher than that of Nb-doped TiO\(_2\), its HER performance was severely suppressed by its low conductivity, which will be presented in Figure 4.11. Therefore, it is suggested that the elevated electrochemical HER of TiO\(_2\) not only originate from the increased intrinsic conductivity and the charge carrier density, but also the modified intrinsic electrocatalytic properties that needed to be further clarified.
Figure 4.8 Electrochemical impedance spectra of different electrodes at −0.3 V versus eversible hydrogen electrode (RHE) (inset is the full range measurement).

Figure 4.9 CV curves of different samples under scanning rate ranging from 20 mV/s to 180 mV/s.

4.6 Determination of the origin of the electrochemical HER activity of OV-TiO₂

4.6.1 Electrical conductivity

Electrical conductivity and the number of electrocatalytic sites are considered to be of great significance for the catalytic performance of electrocatalysts. First of all, five-probe Hall effect measurements were carried out to reveal the conductivities of all the
TiO$_2$ single crystals, as shown in the five probes configuration used in the PPMS measurement in Figure 4.10.

![Figure 4.10](image)

Figure 4.10 The holder used in PPMS measurement and the five probes configuration used in the PPMS measurement.

The electron density of $n$-type semiconductors has an inversely proportional relationship with the Hall coefficient ($R_H$) as $n = -1/(e \cdot R_H)$. As shown in Figure 4.11, OV-high TiO$_2$ had an electrical resistivity of $80.0 \times 10^{-3} \ \Omega \cdot m$ that is lower than that of the OV-low TiO$_2$ ($94.0 \times 10^{-3} \ \Omega \cdot m$). The charge carrier density in OV-high TiO$_2$ ($1.9 \times 10^{17} \ \text{cm}^{-3}$) is about 40 times higher than that in the OV-low TiO$_2$ ($4.8 \times 10^{15} \ \text{cm}^{-3}$). The conductivities of both reduced TiO$_2$ samples are believed to arise from the mid-gap state induced by OVs. The reference Nb-doped TiO$_2$ single crystal exhibits the highest electrical conductivity of $40.6 \times 10^{-3} \ \Omega \cdot m$ and the highest charge carrier density.
of \(3.2 \times 10^{17}\ \text{cm}^{-3}\) among all the samples. The weak electrocatalytic activity of the reference Nb-doped TiO\(_2\) single crystal, however, demonstrates that good electrical conductivity is inadequate to enable TiO\(_2\) activity towards the HER in alkaline media.

Figure 4.11 Hall resistivity measurements of different samples. The Hall coefficient \(R_H\) was determined by fitting the slope of the curve of the Hall resistivity vs. magnetic field.

4.6.2 Electrochemical activate sites

In order to reveal the catalytic process associated with active sites at the atomic level, STM investigations were carried out on the OV-high TiO\(_2\) (110) single crystal. As shown in Figure 4.12, all the adsorbed H\(_2\)O molecules reside on OV sites, as confirmed by the adsorption dynamics observed in Figure 4.12 (a) and (b). OHs also appeared on the OV sites after dissociation of H\(_2\)O molecules, as observed in the dynamic processes in Figure 4.13. This phenomenon suggests that surface OVs are highly active towards adsorbing and dissociating residual H\(_2\)O molecules in UHV.
Figure 4.12 In-situ STM studies on electrocatalytic dynamics occurring on TiO$_2$(110) surface associated with oxygen vacancies. (a) STM image of the partially hydroxylated TiO$_2$ surface, with the OVs indicated by light blue arrows (15 nm × 15 nm, 1.2 V, 20 pA). (b) STM image of the same region of (a), with the OVs mostly filled by H$_2$O (15 nm × 15 nm, 1.2 V, 20 pA).
Figure 4.13 (a) STM image of an individual Ad-H$_2$O at an OV site, with another OV included as a reference point (3 nm × 6 nm, 1.2 V, 10 pA). (b) STM image of the two OHs from the dissociation of Ad-H$_2$O at the OV site (1.2 V, 10 pA). (c) STM image of the same area in a and b, in which an OH was removed through a 2.5 V pulse by the STM tip (1.2 V, 10 pA).
Figure 4.14 (a) STM image of the reduced TiO$_2$ surface with two individual OVs in the empty-state (1.2 V, 20 pA). (b) STM image of the same region of (a), but in the filled-state, with Ti$^{3+}$ ions indicated by red arrows (-2.3 V, 10 pA).

In addition, each OV induces two surrounding Ti$^{3+}$ ions, which was revealed in STM images taken with negative sample bias (filled-state), as shown in Figure 4.14. Recent investigations pointed out that the Ti$^{3+}$ ions in reduced TiO$_2$ exhibit polaron behavior.$^{[34-36]}$ This enables Ti$^{3+}$ ions to rapidly hop across the nearby lattice in rutile, and thus, leads to the increase of the conductivity of the reduced rutile TiO$_2$. Since the electrical conductivity of reduced TiO$_2$ is proportional to the concentration of Ti$^{3+}$ ions, this supports the proposition that the OV-high TiO$_2$(110) single crystal possesses higher conductivity than the OV-low sample. In order to simulate electrocatalytic HER processes, we applied a sample bias to allow the STM tip to act as an electron donator to the OV-high TiO$_2$(110) single crystal surface. Both Ad-H$_2$O and OHs disappeared from the sample surface when the bias was higher than the threshold of 2.0 V, as shown in Figure 4.15 (a) and (b). Meanwhile, the OVs at corresponding sites were also healed. This indicates that hydrogen desorption of Ad-H$_2$O and OHs occurred on the OV-high TiO$_2$(110) surface at the cost of consumption of OVs. In this case, the HER activity of
reduced TiO$_2$(110) single crystal is expected to be depressed gradually with a decreasing concentration of OVs. Nevertheless, this contradicts our cycling stability results, in which the OV-high TiO$_2$(110) surface exhibited excellent stability and durability, suggesting that OVs in the surface are not adequate to drive the electrocatalytic HER constantly and steadily, although they are active towards adsorbing H$_2$O molecules and OHs.

Figure 4.15 STM image of the partially hydroxylated TiO$_2$ surface, with OVs, OHs, and Ad-H$_2$O appearing on the surface (1.2 V, 20 pA). (f) STM image of the same region of c after the OHs and Ad-H$_2$O were removed by the last scan with a tip bias of 2.5 V. (1.2 V, 20 pA).
4.6.3 DFT calculation of the Gibbs free energy

The origins of the electrocatalytic HER activity of the reduced TiO$_2$(110) surface in alkaline media was further revealed by DFT calculations, in terms of thermodynamics and kinetics. The surface structures were modeled according to STEM and STM results obtained on TiO$_2$(110) surface with OVs.

The calculation methods for the hydrogen evolution reaction (HER) in alkaline solutions are summarized as follows:

By considering the standard hydrogen electrode as the reference potential and hydrolysis of water in the solution, the free energy of reactions (4.1) and (4.2) is set to zero because they are in equilibrium. Therefore, the free energy of (H$^+$ + e$^-$) corresponds to that of $\frac{1}{2}$ H$_2$ (1 bar, 298 K) and the free energy of (OH$^-$ – e$^-$) is calculated according to the free energy of H$_2$O and (H$^+$ + e$^-$),

\[
(H^+ + e^-) \rightarrow \frac{1}{2} H_2 \quad (4.1) \\
H_2O \rightarrow (H^+ + e^-) + (OH^- – e^-) \quad (4.2)
\]

We used gas-phase H$_2$O at 0.035 bar as the reference state, because at this pressure, gas-phase H$_2$O is in equilibrium with liquid water at 300 K. The calculated free energies of the H$_2$O, (H$^+$ + e$^-$), and (OH$^-$ – e$^-$) are listed in Table 4.1.

The Gibbs free energy of the intermediates were calculated as$^{[37]}$

\[
\Delta G = \Delta E + \Delta ZPE - T\Delta S \quad (4.3)
\]

where $\Delta E$ is the binding energy of intermediates which is defined as the reaction energies of the reactions

\[
\begin{align*}
H_2O + * &\rightarrow OH^* + H^* \quad (4.4) \\
H_2O + * &\rightarrow OH^* + \frac{1}{2}H_2 \quad (4.5) \\
\frac{1}{2}H_2 + * &\rightarrow H^* \quad (4.6)
\end{align*}
\]
ΔZPE and ΔS can be obtained from the vibrational frequency $v_i$, which are the changes in zero point energies (ZPE) and entropies due to the reaction, respectively. All the parameters have been taken from DFT calculations.

Zero point energies are calculated as follows,

$$ZPE = \sum_i \frac{1}{2} h v_i \quad (4.7)$$

where $i$ is the degree of freedom for the molecule, and $n$ is the number of atoms in the molecule.

Entropies are calculated from the sum of the translational entropy $S_t$, the rotational entropy $S_r$, and the vibrational entropy $S_v$ as follows:

$$S = S_t + S_r + S_v \quad (4.8)$$

$$S_t = Nk_B \ln \left( \frac{8\pi^3 (2\pi k_B T)^{3/2}}{m} \right) \left( \frac{V}{N} \right)^{1/2} + \frac{3}{2} \right) \quad (4.9)$$

$$S_r = Nk_B \left( \ln \frac{8\pi^3 (2\pi k_B T)^{3/2}}{m} \right) \left( \frac{V}{N} \right)^{1/2} + 1 \right) \quad (4.10-1)$$

$$S_v = \sum_i Nk_B \left[ \frac{h v_i}{e^{h v_i/k_B T} - 1} - \ln \left( 1 - e^{-h v_i/k_B T} \right) \right] \quad (4.11)$$

where $k_B$, $N_A$, and $h$ are the Boltzmann constant, Avogadro constant, and Planck constant, respectively. $N$, $m$, $V$, $T$, $I$, and $\sigma$ are the number of particles, and the mass, volume, temperature, moment of inertia, and symmetry number of the molecules, respectively. Otherwise, the entropies of intermediates are calculated by the vibrational entropy $S_v$, because no translational or rotational behaviors can be found for an adsorbed molecule. The calculated ZPE and S of free H$_2$O, H$_2$, and (OH$^-$ - e$^-$) are listed in Table 4.1.
At a pH different from 0, we can correct the free energy of H$^+$ ions by the concentration dependence of the entropy: $\Delta G_{pH} = -kT \cdot \ln[H^+] = kT \cdot \ln 10 \cdot pH$. In our work, pH is 14 and $\Delta G_{pH} = 0.83$ eV.

The effect of a bias $\Delta G_U$ was imposed on each step by including an electron in the electrode as an $-eU$ term, where $U$ is the electrode potential relative to the standard hydrogen electrode. Therefore, the reaction free energy of processes was calculated as:

$$\Delta G_{(U,pH)} = \Delta G + \Delta G_{pH} + \Delta G_U \ (4.12)$$

As is shown in the reactions of the HER in alkaline solution,

Volmer: $\text{H}_2\text{O} + e^- \rightarrow \text{H}^+ + \text{OH}^- \ (4.13)$

Heyrovsky: $\text{H}_2\text{O} + e^- + \text{H}^+ \rightarrow \text{H}_2 + \text{OH}^- \ (4.14)$

Tafel: $2\text{H}^+ \rightarrow \text{H}_2 \ (4.15)$

We include the effects of pH and U on steps involving (OH$^-$ - e$^-$). The free energies of possible steps (such as water splitting, hydroxide adsorption, hydroxide desorption, and hydrogen production) were calculated and compared to find out the most optimal path in our calculation. As a result, the reactions in HER and corresponding free energies under applied potential $U$ and pH can be written as:

Volmer 1 - water splitting

$$\text{H}_2\text{O} + \text{M} \rightarrow \text{H}^+ + \text{OH}^+$$

$$\Delta G_1 = \Delta G (\text{H}^+ + \text{OH}^+)$$

Volmer 2 - OH$^+$ desorption

$$\text{OH}^+ \rightarrow (\text{OH}^- - e^-) + \text{M}$$

$$\Delta G_2 = -\Delta G (\text{OH}^+) + eU + 0.83$$

Heyrovsky

$$\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{H}_2 + (\text{OH}^- - e^-) + \text{M}$$

$$\Delta G_3 = -\Delta G (\text{H}^+) + eU + 0.83$$
Tafel

$$2H^* + M \rightarrow H_2\uparrow$$

$$\Delta G_4 = -\Delta G(2H^*)$$

Here, M represents the catalyst, which can be a TiO$_2$(110) surface with surfOV and subOV, only subOV, or subOV with O$_{br}$-H surface. The calculation results of main reaction pathway are listed in Table 4.1.

Table 4.1. Binding energies, entropies, and zero point energies contribution to Gibbs free energy of main reaction pathway. subOV + O$_{br}$-H* is regard as M.

<table>
<thead>
<tr>
<th>subOV + O$_{br}$-H*</th>
<th>$\Delta E$</th>
<th>ZPE</th>
<th>$\Delta ZPE$</th>
<th>TS</th>
<th>$T\Delta S$</th>
<th>$\Delta ZPE - T\Delta S$</th>
<th>$\Delta G$ (pH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>0.566</td>
<td>0</td>
<td>0.534</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\frac{1}{2}$ H$_2$</td>
<td>0.133</td>
<td></td>
<td>0.201</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>OH$^-$ - e$^-$</td>
<td>0.433</td>
<td></td>
<td>0.333</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H$_2$O$^*$</td>
<td>-0.932</td>
<td>0.631</td>
<td>0.065</td>
<td>0.020</td>
<td>-0.514</td>
<td>0.579</td>
<td>-0.353</td>
</tr>
<tr>
<td>H$^+$ + OH$^-$</td>
<td>-0.735</td>
<td>0.538</td>
<td>-0.028</td>
<td>0.009</td>
<td>-0.525</td>
<td>0.497</td>
<td>-0.238</td>
</tr>
<tr>
<td>H$^+$ + (OH$^-$ - e$^-$)</td>
<td>-0.600</td>
<td>0.671</td>
<td>0.105</td>
<td>0.333</td>
<td>-0.201</td>
<td>0.306</td>
<td>-0.294</td>
</tr>
<tr>
<td>$\frac{1}{2}$H$_2$ + (OH$^-$ - e$^-$)</td>
<td>0.566</td>
<td>0</td>
<td>0.534</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.83</td>
</tr>
</tbody>
</table>
Figure 4.16 DFT calculations reveal roles of oxygen vacancies in electrocatalysis on TiO$_2$(110) surface. (a) Free energy pathways of the relevant reaction intermediates in alkaline media on the reduced TiO$_2$ with both surfOV and subOV, with the OV's marked as solid black circles. (b) Compare of HER free energy of pristine TiO$_2$ and reduced TiO$_2$ with subOV and O$_{br}$H$^*$ (an onset potential of U$_{RHE} = -1.15$ V was applied for both catalysts).

Therefore, based on our calculated, the Free energy pathways of the relevant reaction intermediates in alkaline media on the OV-TiO$_2$ with both surfOV and subOV, is shown in Figure 4.16. It was found that water molecules prefer to be dissociated at surface OV (surfOV) site in initial stage (step 1). The produced hydrogen atoms are favorable towards combing in pairs and forming hydrogen molecules (step 2 to 3). All the reaction steps are exothermic processes. This supports our hypothesis that the surface OVs are easily to be healed during the electrochemical reaction. Hence, it indicates that surfOVs were not sustainable which agrees with STM. HER pathway on the reduced TiO$_2$ with sublayer OV (subOV), as well as the pristine TiO$_2$ were further calculated, as shown in Fig. 4.16 (b). Hydrogen desorption reaction (Heyrovsky
reaction) step between intermediate 2 and intermediate 3 is determined to be the rate-limiting step with the largest free energy difference for both pristine TiO₂ and reduced TiO₂. The pristine TiO₂ needs a theoretical potential of \( U_{\text{RHE}} = -1.33 \, \text{eV} \) to overcome this energy barrier. In contrast, the potential barrier can be effectively lowered on the reduced TiO₂ to enable all HER reaction steps to be exothermic and energetically favorable, due to the presence of subOV. This has been confirmed experimentally in our electrocatalytic HER process, in which onset potential for HER in reduced TiO₂ was significantly decreased. Therefore, the theoretical calculations suggest that the electrocatalytic HER activity of reduced TiO₂(110) single crystal mainly originates from subOVs, which can effectively promote the hydrogen desorption capability and lower the overpotential of HER in alkaline media.

Figure 4.17 Optimized pathway of the HER in alkaline media on the reduced TiO₂ with surfOv and subOV based on the free energy calculation.

Figure 4.17 gives the detailed optimized overall pathway of the HER in alkaline media on the OV-TiO₂ with surfOv and subOV based on the free energy calculation, with all the intermediates listed below:

Intermediates

1: \( \text{TiO}_2\text{-surfOV-subOV} + \text{H}_2\text{O} \rightarrow \text{TiO}_2\text{-subOV} + \text{surfOV-H}_2\text{O}^* \)

2: \( \text{TiO}_2\text{-subOV} + \text{surfOV-H}_2\text{O}^* \)
3: TiO$_2$-subOV + O$_{br}$-H* + Ti-H*

4: TiO$_2$-subOV + H$_2$

5: TiO$_2$-subOV + Ti$_{5C}$-H$_2$O*

6: TiO$_2$-subOV + Ti$_{5C}$-OH* + O$_{br}$-H*

7 and 11: TiO$_2$-subOV + O$_{br}$-H* + OH$^-$

8 and 12: TiO$_2$-subOV + 2O$_{br}$-H* + Ti$_{5C}$-OH*

9 and 13: TiO$_2$-subOV + 2O$_{br}$-H* + OH$^-$

10 and 14: TiO$_2$-subOV + O$_{br}$-H* + OH$^-$ + H$_2$

15: TiO$_2$-subOV + H$_2$

All reactions are written as:

a. TiO$_2$-surfOV-subOV:

Volmer (1-2-3)

$$\text{TiO}_2\text{-surfOV-subOV} + \text{H}_2\text{O} \rightarrow \text{TiO}_2\text{-subOV} + \text{surfOV-H}_2\text{O}^*$$

$$\text{TiO}_2\text{-subOV} + \text{surfOV-H}_2\text{O}^* \rightarrow \text{TiO}_2\text{-subOV} + \text{O}_\text{br}-\text{H}^* + \text{Ti}_{5C}\text{-H}^*$$

Tafel (3-4)

$$\text{TiO}_2\text{-subOV} + \text{O}_\text{br}-\text{H}^* + \text{Ti}_{5C}\text{-H}^* \rightarrow \text{TiO}_2\text{-subOV} + \text{H}_2\uparrow$$

b. TiO$_2$-subOV:

Volmer (4-5-6)

$$\text{TiO}_2\text{-subOV} + \text{H}_2\text{O} \rightarrow \text{TiO}_2\text{-subOV} + \text{Ti}_{5C}\text{-H}_2\text{O}^*$$

$$\text{TiO}_2\text{-subOV} + \text{Ti}_{5C}\text{-H}_2\text{O}^* \rightarrow \text{TiO}_2\text{-subOV} + \text{Ti}_{5C}\text{-OH}^- + \text{O}_\text{br}-\text{H}^*$$

Heyrovsky (6-11)

$$\text{TiO}_2\text{-subOV} + \text{Ti}_{5C}\text{-OH}^- + \text{O}_\text{br}-\text{H}^* \rightarrow \text{TiO}_2\text{-subOV} + \text{O}_\text{br}-\text{H}^* + (\text{OH}^- - \text{e}^-)$$

c. TiO$_2$-subOV + O$_{br}$-H$^+$:

Volmer (11-12-13)

$$\text{TiO}_2\text{-subOV} + \text{O}_\text{br}-\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{TiO}_2\text{-subOV} + 2\text{O}_\text{br}-\text{H}^* + \text{Ti}_{5C}\text{-OH}^*$$
\[
\text{TiO}_2\text{-subOV} + 2\text{O}_\text{br-H}^+ + \text{Ti}_5\text{C}^-\text{OH}^- \rightarrow \text{TiO}_2\text{-subOV} + 2\text{O}_\text{br-H}^+ + (\text{OH}^- - \text{e}^-)
\]
Heyrovsky (13-14)

\[
\text{TiO}_2\text{-subOV} + 2\text{O}_\text{br-H}^+ + \text{H}_2\text{O} \rightarrow \text{TiO}_2\text{-subOV} + \text{O}_\text{br-H}^+ + \text{H}_2\text{↑} + (\text{OH}^- - \text{e}^-)
\]
Tafel (13-15)

\[
\text{TiO}_2\text{-subOV} + 2\text{O}_\text{br-H}^+ \rightarrow \text{TiO}_2\text{-subOV} + \text{H}_2\text{↑}
\]

4.7 Summary

Our study shows that inactive pure TiO₂ rutile(110) single crystal can be activated towards the HER in alkaline media through creating OVs and accompanying Ti³⁺ ions by annealing in UHV. OVs and Ti³⁺ ions in the surface region dominate the electrical conductivity of reduced TiO₂ and the amount of electrocatalytic active sites.

Combining the well-characterized atomic surface structure and theoretical calculations, we conclude that subOVs can promote the electron transfer and hydrogen desorption in the electrocatalytic HER on reduced TiO₂ in alkaline media. Considering that all the electrochemical characterizations were performed on a single crystal sample with atomically flat surface and low specific surface area, the overpotential is expected to be significantly decreased in reduced TiO₂ nanoparticles with a higher density of active sites. Our work helps to elucidate the fundamental mechanism of the electrocatalytic activity of reduced oxides towards the HER, which is of immense fundamental and practical importance towards an in-depth understanding and rational optimization of TMOs as electrocatalysts in alkaline media.

4.8 References


Chapter 5 Tuning electronic structure of BiOBr 2D nanosheets by strain for photocatalysis

5.1 Introduction

The ability to continuously control the electronic structures in photocatalysts is highly desirable for a wide range of energy and environmental applications, including H₂ production by water splitting, carbon fixation, and the elimination of pollution.[1,2] For example, the absorption spectrum and the quantum conversion efficiency of a photocatalyst, which determine its performance, can be modulated by tuning the band gap (Eg), the positions of the VB and the conduction band (CB), and the band dispersion of photocatalysts.[3] In a similar way to chemical composition, strain is a continuous variable that is capable of altering electronic structure. Although strain engineering is a straightforward method, its potential in photocatalysis remains largely under-exploited.

Bismuth oxyhalides BiOX (X = Cl, Br, I) are p-block photocatalysts that have attracted considerable attention due to their unique 2D layered structure and excellent photocatalytic properties under visible light.[4-9] In BiOX, [Bi₂O₂]₂⁺ slabs are interleaved with double halogen atoms slabs by strong electrovalent bonds along the [001] direction, while two closely adjacent slabs of halogen atoms are connected by van de Waals interactions.[10,11] The dispersive VB and CB induced by sp hybridization give rise to high mobility of the photo-induced charge carriers. In addition, the internal electric field resulting from the asymmetric charge distribution between [Bi₂O₂]₂⁺ and the halogen layers facilitates the effective separation of these photo-induced charge carriers, and hence, enables the photocatalytic activity of BiOX.[12-14] Due to their 2D
layered structure, the electronic structure of BiOX compounds is highly sensitive to even a subtle inner strain variation.\textsuperscript{[15]} It is, however, a practical challenge to modulate the photocatalytic properties through fine-tuning the inner strain in nanoscale BiOX. In this work, we illustrate experimentally and theoretically that the photocatalytic performance of BiOBr nanosheets can be tuned by the inner strain effect. The characterizations of photocatalytic degradation and geometric phase analysis (GPA) of the TEM images indicate that the distribution and intensity of the inner strain dominate the photocatalytic activity of BiOBr nanosheets. DFT calculations demonstrate that the strain-modulated photocatalytic properties in BiOBr originate from variation of the intrinsic electronic structure of this photocatalyst.

5.2 Experimental section

In the synthesis procedure, 5 mmol Bi(NO\textsubscript{3})\textsubscript{3}·5H\textsubscript{2}O and 5 mmol cetyl trimethylammonium bromide (CTAB) were added into 100 mL distilled water at room temperature with stirring for 20 min, and then, 1 M NaOH solution was added to the solution to adjust the pH value to 7, 5, 3, and 2 (with the resulting samples denoted as BiOBr-1, BiOBr-2, BiOBr-3, and BiOBr-4, respectively). The mixed solution was stirred for 1 h, and then poured into a 100 mL Teflon-lined stainless autoclave up to 80\% of the total volume. The autoclave was heated at 170 °C for 17 h, and then cooled to room temperature in air. The resulting precipitates were collected, washed with ethanol and deionized water several times, and dried at 80 °C for 10 h.

The morphologies and microstructures of the as-prepared samples were characterized by SEM (Hitachi CS 3400) and TEM (JEOL JEM-3010, operated at 300 kV). In the photo-degradation experiments, BiOBr powder (100 mg) was added to an aqueous solution of Rh B (0.02 mmol/L, 100 mL) in a 150 mL quartz reactor.
Degradation experiments on Rh. B using N-doped P25 TiO₂ nanopowders were also carried out under the same conditions as a reference. For the photo-degradation of MO (10 mg/L, 50 mL), 50 mg catalyst was added to an aqueous solution of MO (10 mg/L, 50 mL) in a 150 mL quartz reactor. All photocatalytic experiments were carried out under irradiation by a 300 W Xe lamp with a filter glass (λ ≥ 420 nm) to remove ultraviolet (UV) light after dark adsorption experiments. The absorption spectra of Rh. B and MO were collected on a Hitachi U3010 UV-Visible (UV-Vis) spectrophotometer. In the photocurrent-time response system, a 300 W Xe lamp with a monochromator and a cut-off filter (λ ≥ 420 nm) was used as the light source. UV-Vis diffuse reflectance spectra were collected on a Cintra-10e spectrometer. The distributions of in-plane strain across the nanosheets were identified by GPA based on the HRTEM images. In this paper, STEM-CELL was used to simulate the distribution of the strain, based on the HRTEM images, by calculating and analysing the fast Fourier transform (FFT) and inverse FFT of the entire images. In the analysis process, the displacement of lattice parameters (u) are determined by calculating and analysing the Fourier transform of the selected image. The strain is then obtained from the derivative of the displacement in the picked direction, and visualized by inverse Fourier transform.

The first-principles calculations were performed using the VASP code. The GGA was applied to treat the exchange correlation energy with the PBE functional. The PAW method was employed to describe the electron-ion interactions. A k-point sampling of 9×9×6 was generated with original Gamma meshes. The cut-off energy for the plane wave basis was 550 eV. The biaxial strain simulations were realized by fixing the x and y axes and optimizing the z axis. Equilibrium geometries were obtained by the minimum energy principle.
5.3 Morphology and structure characterization

Figure 5.1 SEM images of (a) BiOBr-square and (d) BiOBr-circle (scale bar is 1 μm). Cross-sectional TEM images of (b) BiOBr-square and (e) BiOBr-circle (scale bar is 200 nm); insets are the HRTEM images of the cross-sections, where both samples show layer structure along the c-axis (scale bar is 10 nm). HRTEM images of (c) BiOBr-square and (f) BiOBr-circle, with the corresponding SAED patterns as the insets, indicating that both samples have the (001) face exposed (scale bar is 10 nm⁻¹ and 5 nm⁻¹ for the insets).

Figure 5.1 shows two typical morphologies of BiOBr nanosheets, square-shaped (also assigned as BiOBr-1) and circle-shaped BiOBr (BiOBr-4), which were fabricated by hydrothermal reaction with different pH values. We found that the BiOBr nanosheets underwent a morphology transition from square-like to circle-like when the pH value was decreased. The BiOBr nanosheets are several micrometres in size. The thicknesses of the BiOBr-square and BiOBr-circle nanosheets are 31 nm and 22 nm, respectively, as revealed by TEM in Figure 5.1 (a) and (b). The insets demonstrate the layered structure of the BiOBr nanosheets. The interlayer distance is approximate 0.8 nm for both samples. As shown in Figure 5.1 (c)-(f), the d-spacing of 0.27 nm indicates
that the (110) face is along the in-plane BiOBr nanosheets. The corresponding insets show the selected area electron diffraction (SAED) patterns, in which the marked spots can be indexed as (200) face, (110) face and (1-10) face. Hence, the exposed surfaces can be identified as {001} facets for both the BiOBr-square and the BiOBr-circle nanosheets.

5.4 Characterization of strain in BiOBr 2D nanosheets

By carefully examining the X-ray diffraction (XRD) patterns, obvious diffraction peak shifts could be identified. Figure 5.2 shows the XRD patterns of the as-prepared BiOBr nanosheets. All the samples (labelled as BiOBr-1 to BiOBr-4) prepared by the hydrothermal method with different pH values are well-crystallized single-phase nanopowders. The diffraction patterns can be indexed to the tetragonal structure (P4/nmm(129)) according to the standard data (PDF card #09-0393). By precisely controlling the concentration of NaOH, the diffraction peaks can be shifted gradually in accordance with the pH value of the precursors, as shown in Figure 4.2 (a). In particular, the (110) peak and the (004) peak demonstrate a clear upshifting with increasing pH value, as shown in Figure 5.2 (b)-(d). BiOBr possesses a typical 2D layered crystal structure, in which [Bi₂O₂]^{2+} slabs are interleaved with double bromine atom slabs by strong electrovalent bonds along the [001] direction, as shown in the insets of Figure 5.2 (c) and (d). The diffraction peak shift indicates the presence of in-plane strain in BiOBr. The change in the corresponding interplanar crystal spacing, identified by the refined cell parameters obtained using MDI Jade 5.0 (Materials data, Inc., Livermore, CA, 1999), was used to estimate the degree of in-plane strain in BiOBr by comparing it with the theoretical $d$-value. As shown in Figure 5.2 (c) and (d), in contrast to the BiOBr-4 sample, which exhibits tiny strain, BiOBr-1 shows a much
higher degree of compressive strain for both the {110} and the {001} facets. More importantly, our results indicate that by carefully controlling the pH value during sample preparation, the crystal strains were gradually changed for the BiOBr nanosheets by a facile chemical method.

![Figure 5.2](image)

**Figure 5.2** (a) XRD patterns of BiOBr samples fabricated with different pH values. (b) Local areas of (110) and (004) peaks of BiOBr, where obvious shifts of the peaks are observed, which are indicated for different BiOBr samples. (c) and (d) Plots of the changes in the peak positions and the relative tensile strain compared with the theoretical crystal structure of the (110) and (004) faces, respectively; insets are schematic illustrations of the BiOBr crystal structure.
Figure 5.3 TEM images of (a) BiOBr-square and (c) BiOBr-circle (scale bars are 1000 nm). Strain simulation of (b) BiOBr-square and (d) BiOBr-circle based on HRTEM (scale bars are 10 nm). The internal strain distributions are in the \(xy\)-direction (\(E_{xy}\)), the \(x\)-direction (\(E_{xx}\)) and the \(y\)-direction (\(E_{yy}\)), with the scale for the whole image area.

In order to reveal the details of the morphology dependence of the inner strain, we carried out TEM characterization and GPA simulation based on the HRTEM images, as shown in Figure 5.3.\(^{[16-18]}\) The in-plane wrinkles observed in the TEM images of the BiOBr-square nanosheets reflect the existence of a large inner strain, while the BiOBr-circle sample exhibits a relatively strain-free character, as shown in Figure 5.3 (a) and (c). Figure 5.3 (b) and (d) show the inner strain distribution maps of the BiOBr nanosheets in the \(xy\)-direction (\(E_{xy}\)), the \(x\)-direction (\(E_{xx}\)), and the \(y\)-direction (\(E_{yy}\)), respectively, as obtained by strain simulation. The inhomogeneous compressive strain...
distribution in the BiOBr-square nanosheets is reflected by the severe local lattice distortions across the whole surface in Figure 5.3 (b). In contrast, the BiOBr-circle nanosheets exhibit a quite uniform strain distribution, and this sample shows much less lattice distortion in the strain maps in Figure 5.3 (d). It should be noted that the strain difference across the BiOBr-square nanosheets is higher than that across the BiOBr-circle nanosheets. For example, the strain in the BiOBr-square sample varies from 0.73 to 1.29 ($E_{xy}$), from 0.78 to 1.21 ($E_{xx}$), and from 0.80 to 1.16 ($E_{yy}$), while in BiOBr-circle, it varies from 0.88 to 1.17 ($E_{xy}$), from 0.87 to 1.10 ($E_{xx}$), and from 0.93 to 1.08 ($E_{yy}$). These results confirm that the inner strain of the BiOBr nanosheets can be varied by the morphology, which can be precisely tuned by the fabrication conditions.

5.5 Characterization of photocatalytic activity of BiOBr 2D nanosheets

Firstly, UV-Vis diffuse reflectance spectra of the BiOBr nanosheets with different strains were carried out to determine their band gap, which has a significant impact on their light absorption ability. The band gap of semiconductor can be determined by the Tauc formula,

$$\alpha h\nu = A(h\nu - E_g)^n$$ \hspace{1cm} (5.1)

$$E_g = \frac{1240}{\lambda}$$ \hspace{1cm} (5.2)

Here, $\alpha$, $\nu$, $E_g$, $A$, $n$, and $\lambda$ are the absorption coefficient, the incident light frequency, the band gap, a constant, an integer, and the absorption edge, respectively. Firstly, the approximate $E_g$ can be calculated by Equation 5.2, and then $\ln(\alpha h\nu)$ vs. $\ln(h\nu-E_g)$ is plotted; thus, by refining the slope of the straightest line near the band edge we can obtain the value of $n$. Secondly, $(\alpha h\nu)^{2/n}$ vs. $h\nu$ is plotted, and then the band gap $E_g$ is evaluated by drawing an extension line to the $h\nu$ axis intercept. Finally, the accurate
value of $E_g$ of BiOBr-square is calculated as 2.68 eV, and 2.82 eV is calculated for BiOBr-circle. This indicates that the inner strain has a significant effect on the band gap of BiOBr.

As shown in Figure 5.4, the BiOBr samples exhibit excellent photocatalytic performance in Rh B degradation. Their photocatalytic activities are higher than for N-doped P25 TiO$_2$ nanopowders. The low-strain BiOBr-circle sample shows the highest activity among all the samples, and it demonstrates almost 100% degradation of Rh B within 30 min. As demonstrated in Figure 5.4 (c), the apparent first-order rate constant ($k$) for BiOBr-circle is almost twice those for BiOBr-square and the N-doped P25 TiO$_2$ nanopowders. Similar results were also observed for degradation of other dyes, such as MO, as shown in Figure 5.4 (d). As shown in Figure 5.4 (e), both the BiOBr-square and the BiOBr-circle samples can degrade phenol under visible light. Again, the BiOBr-circle nanosheets show better visible-light photocatalytic degradation performance on phenol than the BiOBr-square nanosheets. The photocurrent response of the BiOBr samples were measured for several On-Off cycles under visible light irradiation. As shown in Figure 5.4 (f), the photocurrent of the BiOBr samples exhibits a quick response to light irradiation, with the photocurrent sharply decreasing to zero as soon as the light is turned off, while the photocurrent quickly reaches stable values when the light is turned on. The stable photocurrents measured on the BiOBr-square and BiOBr-circle samples under visible light are 0.7 µA and 1.5 µA, respectively. The higher photocurrent of BiOBr-circle than BiOBr-square under visible light suggests that more efficient photoexcited charge carrier separation and less recombination of electron-hole pairs were possibly achieved by decreasing the inner strain in the BiOBr nanosheets.
5.6 DFT of the strain effect on the electronic structure of BiOBr

We carried out DFT calculations in order to reveal the strain effect (both compressive and tensile strains) on the electronic structure of BiOBr, which dominates the photocatalytic properties.\(^{19-21}\) The strain-free and compressive-strained BiOBr show the typical electronic features of an indirect-band-gap semiconductor. It changes to a direct band-gap semiconductor, however, if tensile strain is present in BiOBr. With a 9.1% tensile strain in the BiOBr lattice, the valence band maximum (VBM) of BiOBr moves from the R point to the Z point, while the CBM is still located at the same high symmetry point (Z point) in \(k\)-space. It is found that the \(E_g\) of BiOBr can be modulated by the strain effect, as shown in Figure 5.5 (a). For example, the band gap varies...
between 1.94 eV, 2.12 eV, and 1.27 eV in BiOBr which has 8.8% compressive strain, is free of strain, and has 9.1% tensile strain, respectively. Both compressive and tensile strains lead to a narrowed band gap, which is also observed in the other indirect-band-gap semiconductors.\(^{[22]}\) Figure 5.5 (b) shows the calculated DOS. It is found that the bottom of the CB of strain-free BiOBr is mainly contributed by Bi 6\(p\), and the top of the VB is dominated by Br 3\(p\), O 2\(p\), and Bi 6\(s\) orbitals. While under tensile strain, the contribution of Bi 6\(s\) to the VBM is suppressed.

Figure 5.5 DFT calculations of the band structure of BiOBr with biaxial strain. (a) The left panel models compressive strain, the central panel is for a strain-free sample, and the right is for tensile strain. (b) Calculations of the DOS of BiOBr with different kinds of strain.

Several key factors can affect the photocatalytic activity of BiOBr nanosheets in photocatalytic reactions, which include photon absorption, separation of photoexcited carriers, and surface area. Our UV-Vis diffuse reflectance spectra results demonstrate that the band gap of BiOBr-square \((E_g = 2.68 \text{ eV})\) is smaller than that of BiOBr-circle \((E_g = 2.82 \text{ eV})\). BiOBr-square is, therefore, expected to have a broader range of light absorption, in contrast to BiOBr-circle. BET measurements reveal that the BiOBr-square sample exhibits a larger surface area of 7.03 m\(^3\)/g compared to BiOBr-circle (4.49 m\(^3\)/g) (Table 5.1). It is interesting, however, that the photocatalytic measurements indicate that the photocatalytic activity of BiOBr-square is much lower than that of BiOBr-circle. This is because the photoexcited charge separation in BiOBr determines
the overall photocatalytic activity in the photocatalytic process, which was also reported in previous works.[23,24] As shown in Figure 5.4 (f), the photocurrent measurements suggest that the charge separation is indeed more efficient in BiOBr-circle nanosheets than in BiOBr-square nanosheets. Based on the DFT calculation results, we believe that the electronic structure of the BiOBr-circle sample may facilitate the separation of photoexcited charge carriers. It was found that the interactions between Br atoms and [Bi₂O₂]²⁺ slabs mediated by weak van de Waals coupling are tunable by the strain effect. In other words, the band symmetry of BiOBr can be modulated by strain through tuning the electronic interaction between the Br atoms and the [Bi₂O₂]²⁺ slabs. The dramatic changes in the band symmetry, e.g. from direct to indirect band gap or the change of energy dispersion due to the strain, would affect the separation of photoexcited charge carriers. The electron-hole recombination occurring in indirect semiconductors typically requires the emission of multiple phonons to accommodate the energy and momentum differences between the CB and the VB. An appropriate rearrangement of the electronic symmetry, for instance, in the BiOBr-circle sample, may tune the momentum mismatch and improve electron-hole separation. Moreover, the VB and CB in strain-free BiOBr are more dispersive, which is expected to lead to a high mobility of photoexcited charge carriers. In the case of the BiOBr-square nanosheets, their electronic structure modifications by the strain effect might depress the separation of photoexcited charge carriers, and consequently, weaken the photocatalytic performance. In addition, strain also leads to the formation of structural defects in 2D materials. In BiOBr-square nanosheets, a large strain of 1.8 % is verified by the XRD and GPA results. It is believed that strain-induced defects will act as recombination centres for photoexcited electrons and holes, and also depress the quantum conversion efficiency of strained BiOBr-square nanosheets.
Table 5.1 BET test of the surface area of different BiOBr samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET (m$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiOBr-1</td>
<td>7.03</td>
</tr>
<tr>
<td>BiOBr-2</td>
<td>7.85</td>
</tr>
<tr>
<td>BiOBr-3</td>
<td>5.47</td>
</tr>
<tr>
<td>BiOBr-4</td>
<td>4.49</td>
</tr>
</tbody>
</table>

5.7 Summary

In summary, the strain effect on the photocatalytic activity of BiOBr nanosheets with highly reactive {001} facets exposed was studied. The XRD, TEM, and strain tensor simulation results reveal that the intensity and distribution of inner strain in the BiOBr nanosheets can be modulated by adjusting the pH value in the synthesis reaction. It is found that the strain effect can effectively tune the photocatalytic activity of BiOBr nanosheets in dye degradation. Our work suggests that strain engineering could be an effective approach to controlling the electronic structure of semiconductors for further enhancement of their efficiency in converting light into other forms of energy.

5.8 References


Chapter 6 Construction of 2D lateral pseudo-heterostructures by strain engineering

6.1 Introduction

Discontinuities at interfaces in heterogeneous structures can lead to exciting and possibly non-trivial properties, due to broken symmetries at the interfaces. Through constructing heterostructures, one can feasibly engineer and manipulate electronic, optical, and magnetic phases at so-called heterointerfaces, and thus, generate unusual properties and new phenomena.\textsuperscript{[1,2]} Numerous breakthroughs have been achieved by taking advantage of vertical heterostructures in previous studies. For examples, naturally formed heterostructures give birth to high-temperature superconductivity (High-\(T_c\)) and topological states in copper-oxide-based superconductors and topological insulators, respectively.\textsuperscript{[3,4]} Artificial heterostructures were also constructed in laminated LaAlO\(_3\)/SrTiO\(_3\) films, in which magnetic order and superconductivity surprisingly coexist.\textsuperscript{[5,6]} Very recently, fabrication of vertical van de Waals (vdW) heterogeneous structures were successfully achieved by using atomically thin layer materials, including graphene and \(h\)-BN, which drew immediate attention.\textsuperscript{[7-10]} Besides vertical heterostructures, lateral heterostructures with two materials joined laterally have also drawn great attention.\textsuperscript{[11]} The research in this field was boosted soon after single-layer-thick 2D lateral heterostructures were successfully fabricated, as they possess controllable band-offset tuning and can be used in electronics, optoelectronics, and catalysis. Lateral interfaces in 2D lateral heterostructures are constructed from covalent bonds and not linked by vdW forces. Less electron and phonon scattering centers are expected across the interface. Electron hopping and band alignment in such
lateral heterostructures are therefore less affected by the interfaces, which, in turn, promotes charge carrier transport across the lateral interfacial junctions. These advantages of 2D lateral heterostructures have been observed and verified in graphene/h-BN lateral heterogeneous structures. In these systems, high field-effect mobility of charge carriers and low hysteresis behavior have been demonstrated\cite{12,13} 2D lateral heterostructures based on two different transition-metal dichalcogenides (TMD) were also successfully fabricated, exhibiting lateral p-n diodes behaviors or staggered band alignment. A broad range of applications based on 2D lateral TMD heterostructures, therefore, have been proposed, such as logic circuits, field-effect transistors, and photodetectors\cite{14-16}.

Despite their appealing advantages, great challenges remain in constructing 2D lateral heterostructures with the desired properties. A clean and atomically sharp interface is the essential requirement to achieve exotic characteristics. To achieve this goal, sophisticated and costly manufacturing methods such as MBE, lithography, and chemical vapor deposition are necessary for fabricating these high-quality interfaces\cite{11,17}. It is still extremely difficult to achieve 2D lateral heterostructures with a large area, instead, most epitaxially-grown samples possess small heterogeneous domains. The other limitation originates from lattice mismatch at the lateral heterointerface. The candidate materials for 2D lateral heterostructures must have similar crystal structures and lattice constants. This is the reason why very few 2D lateral heterostructures have been reported so far\cite{18}. An alternative strategy to overcome these limitations is to develop a “lateral pseudo-heterostructure”\cite{19,20}. Generally, the pseudo-heterostructures have a single chemical component but show spatial variation in their physical properties, which offers a promising way to build 2D
systems that show the functionalities of 2D lateral heterostructures but overcome the problems of lattice mismatch.

Here, we report a 2D lateral pseudo-heterostructure with an electronic heterogeneous interface constructed from single-component BiOBr 2D nanosheets by strain engineering. As a typical bismuth oxyhalide (BiOX, where X = Cl, Br, I),\textsuperscript{21,22} BiOBr has great potential for use in photoenergy conversion applications, owing to its indirect band gap of 2.8 eV.\textsuperscript{23-26} Taking advantage of their strain-sensitive electronic structure, few-layer-thick BiOBr nanosheets were successfully prepared with controlled spatial distributions of local electronic structures by manipulating the strain distribution. The position and characteristics of the electronic heterogeneous interface can also be tuned by adjusting the strain distribution in the nanosheets. Effective separation of charge carriers at the electronic heterointerface is then demonstrated in this lateral pseudo-heterostructure, owing to the appropriate band alignment at the electronic heterogeneous interface. Its excellent photoresponse and enhanced photocurrent suggest that such lateral pseudo-heterostructures are potential candidates for superior optoelectronic devices.

6.2 Experimental section

To synthesize BiOBr nanosheets, 5 mmol Bismuth nitrate pentahydrate and 5 mmol CTAB were, respectively, added into 100 mL distilled water at room temperature. Sodium hydroxide solution (1 M) was added to the mixed solution to adjust the pH value. The mixed solution was then stirred for 1 h, and poured into a 100 mL Teflon-lined stainless autoclave up to 80% of the total volume. In the hydrothermal reaction, the sealed autoclave was heated at 170 °C for 17 h, and then cooled in air. The resulting precipitates were collected, washed with ethanol and deionized water several times,
and dried at 80 °C for 10 h. Bismuth nitrate pentahydrate, Sodium hydroxide, and CTAB were purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC). All reagents used in this work were of analytical grade and were used as received without any further purification.

The morphologies and microstructures of the as-prepared samples were characterized by SEM (JEOL JSM-7500FA) and HAADF images were obtained by STEM (JEOL JEM-ARM200F). A commercial AFM (Asylum Research MFP-3D) was used to measure the morphology and surface potential of the BiOBr nanosheets by scanning Kelvin probe microscopy (SKPM). A Pt/Ir coated n-silicon probe with resonance frequency of 45-115 kHz and force constant of 0.5-0.95 M/m was used in the AFM measurements. BiOBr powders were distributed on gold (50 nm) coated silicon substrates. Before characterization of the surface potential of BiOBr samples, the surface potential of the Pt/Ir tip was calibrated on a standard Si wafer coated with Au film. Raman mapping investigations were carried out with a confocal Raman spectrometer (Horiba Xplora) using a 532 nm wavelength laser as the excitation source.

The first-principles calculations were performed using the VASP code. The GGA was applied to treat the exchange correlation energy with the PBE functional. The PAW method was employed to describe the electron-ion interactions. A k-point sampling of a $9 \times 9 \times 6$ grid was generated with original Gamma-centred meshes. The cut-off energy for the plane wave basis was 550 eV. The biaxial strain simulations were realized by fixing the x and y axes and optimizing the z axis. Equilibrium geometries were obtained by the minimum energy principle.

A pair of electrical contacts (Ti/Au, 5/50 nm thick) was fabricated on the a SiO$_2$/Si surface, by standard electron beam lithography, using a poly(methyl methacrylate) resist and the lift-off method. BiOBr nanosheets were dispersed in ethanol and then
dropped on the as-prepared surface followed by air-drying at 60 °C. Flakes suitable for electrical characterization were identified by an optical microscope. Photocurrent measurements were performed in vacuum at room temperature, using a probe station connected to a semiconductor parameter analyser (Agilent B1500). The drain bias of 10 V and a gate bias of 80 V have been applied. The wavelength of the light source was 450 nm. The power of the light was measured to be 50 mW·cm⁻².

6.3 Structure characterization of BiOBr nanosheets

![AFM images of BiOBr nanosheets](image)

Figure 6.1 (a) AFM images of BiOBr-circle nanosheets. (b) and (c) AFM images of BiOBr nanosheets synthesized with pH values between 7 and 2. (d) AFM images of BiOBr-circle nanosheets. Scale bars are 1μm.

The morphologies of the BiOBr nanosheets were revealed by SEM and AFM. Figure 6.1 shows the evolution of the morphology of BiOBr nanosheet, which undergo a shape transition from square to circle. They also indicate that BiOBr nanosheets are approximately several micrometers in size. The concentration of hydroxide is thus expected to be the key factor that determines the shape of the 2D BiOBr nanosheets.

Despite their different shapes, all the nanosheets display a layered structure, which is confirmed in the cross-section TEM images in Figure 6.2. The thickness of the BiOBr-square and BiOBr-circle show similar thickness of 15-40 nm, as shown in
Figure 6.3. The large area-to-thickness ratio reflects their 2D nature. The interlayer distances for the BiOBr-square and BiOBr-circle nanosheets are ~0.76 nm and ~0.78 nm, respectively, which correspond to the spacing of BiOBr (001) face. This indicates that the BiOBr nanosheets have a preferred growth orientation normal along the [001] direction.

Figure 6.2 (a) SEM image of BiOBr-square nanosheets. (b) and (c) Cross-sectional TEM images of a single BiOBr-square nanosheet. (d) SEM image of BiOBr-circle nanosheets. (e) and (f) Cross-sectional TEM of a single BiOBr-circle nanosheet.
Figure 6.3. (a) AFM image of BiOBr-square nanosheets. (b) The height profile corresponding to the black line in (a). (c) AFM image of BiOBr-circle nanosheets. (d) The height profile corresponding to the black line in (c).

Figure 6.4 XRD patterns of BiOBr-square and BiOBr-circle powders.
Figure 6.5 EDS mapping of elements (Bi, O, Br) distribution of BiOBr-square and BiOBr-circle nanosheets. All elements uniformly distribute across the surface.

Our XRD, SEM, TEM, and EDS measurements verify that all BiOBr nanosheets are pure phase without any detectable impurities or structural defects, as shown in Figure 6.4 and Figure 6.5.

6.4 Strain induced pseudo-heterostructure

Figure 6.6 shows STEM images of BiOBr nanosheets with both square and circular shape that were collected in HAADF mode. The atomic arrangements of the nanosheets are clearly revealed and demonstrate their 2D single-crystal nature. Interestingly, these BiOBr nanosheets have distinct local atomic features associated with their shapes, especially in the areas close to the edges of the nanosheets. A homogeneous atomic arrangement is observed across the whole BiOBr-square nanosheet, including edge areas, as shown in Figure 6.6 (b). No obvious difference has been found in the atomic fringes across the whole square nanosheet. The corresponding FFT pattern is shown in Figure 6.6 (c) (pattern A across the whole nanosheet). Only one set of patterns can be observed. In contrast, the BiOBr-circle sample exhibits an inhomogeneous atomic arrangement across the nanosheet in Figure 6.6 (e). The areas close to the edge exhibit relaxation in their atomic structures, although the central area retains a similar atomic
arrangement to that in the square nanosheet. The FFT pattern, shown in Figure 6.6 (g), exhibits a group of symmetric spots (pattern B, labelled in green) in addition to the intrinsic spots (pattern A, labelled in yellow). These spots of pattern B with a shorter nearest-neighbor spot distance are attributed to the area close to the edge (Area B) in Figure 6.6 (f). Their presence reflects the considerable lattice relaxation exists in the areas close to the edges, as illustrated in Figures 6.7.

Figure 6.6. (a) HAADF image of BiOBr-square, showing a homogeneous crystal structure (inset: lower magnification to show whole nanosheet). (b) Enlarged image from the selected area in (a). (c) Corresponding FFT pattern of the area in (b). (d) Strain mapping of BiOBr-square by GPA. (e) HAADF image of BiOBr-circle, showing an interface of the pseudo-heterostructure (inset: lower magnification to show whole nanosheet). (f) Enlarged image from the selected area in (e). (g) Corresponding FFT pattern of the area in (f). (h) Strain mapping of BiOBr-square by GPA. In the image of GPA, the blue zones are under compressive strain, the red zones are under tensile strain, and the green zones are not strained.
Figure 6.7 Schematic diagram of the transition of the shape in (001) face exposed BiOBr nanosheets. (a) BiOBr-square with most area of the edge of BiOBr-square are terminated by \{110\} facets and the other small edge area terminated by \{100\} facets. (b) BiOBr-circle nanosheet, without any specific terminated faces. Bi atoms and O atoms are shown as purple and red balls respectively.

These relaxed areas induce a significantly inhomogeneous distribution of inner strain in the BiOBr-circle nanosheets. It should be noted that a sharp interface can be observed between Area A and Area B in the BiOBr-circle nanosheets, as indicated by the dashed lines in Figure 6.6 (e) and (f). This interface can be regarded as a lateral pseudo-heterointerface, because both areas have identical chemical component composition but distinctly different inner strains. (see more TEM images in Figure 6.8 and Figure 6.9) In order to revealing the detailed local strain distribution, we used the GPA method to study both square and circle nanosheets.\textsuperscript{[27,28]} Figure 6.6 (d) and (h) show GPA strain mapping results for the BiOBr-square and the BiOBr-circle nanosheets, respectively. As shown in Figure 6.6 (d), the distribution of local strain is uniform despite the subtle fluctuation in the BiOBr-square nanosheets. Whereas, Figure 6.6 (h) shows that the inner strains of Area A and Area B in the BiOBr-circle nanosheet are different, with a clear interface between these two areas (see more results
in Figure 6.10). Our high resolution TEM (HRTEM) images and GPA suggest that the strain distribution in the BiOBr nanosheets can be manipulated through controlling the concentration of hydroxide (pH value) in the hydrothermal reactions. Lateral pseudo-heterostructures based on inhomogeneous strain distribution can be obtained in a single BiOBr nanosheet.

Figure 6.8 (a) HRTEM images of BiOBr-circle nanosheets, showing clear interfaces between edge area and central area. (b) HRTEM images of BiOBr-square nanosheets. No interfaces are observed in BiOBr-square nanosheets.

Figure 6.9 (a)-(d) TEM images of BiOBr nanosheets showing the change of shape from square to circle with the pH value change from 7 to 2. (e)-(f) HRTEM of BiOBr nanosheets with intermediate shapes between square and circle.
Finally, based on the above experimental results, we propose a possible formation mechanism of the lateral pseudo-heterostructure by reliving the inner strain in BiOBr-circle nanosheets. In this synthesis method, the reactions could be described as follows which were proposed by M. Shang et al.\cite{29}

\[
\begin{align*}
\text{Bi}^{3+} + \text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N-Br} & \rightarrow \text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N-Br-Bi}^{3+} \quad (6.1) \\
\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N-Br-Bi}^{3+} + \text{OH}^- & \rightarrow \text{BiOBr} + \text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+ + \text{H}^+ \quad (6.2)
\end{align*}
\]

CTAB is proposed to act as both the template where BiOBr microplates nucleate and grow, and the Br source. In the aqueous solution, as shown in the schematic diagram
of reaction procedures in Figure 6.11, CTAB is lamellar structure with the surface terminated by Br\(^-\) anions. Mixed Bi\(^{3+}\) cations combine with CTAB at the initial positions of the Br\(^-\) anions, which will further react with OH\(^-\) anions and form multilamellar BiOBr precursors, as illustrated in Equation 6.2. Through adjusting the concentration of OH\(^-\), the reaction speed can be controlled. A higher concentration of OH\(^-\) will result in a higher reaction speed, and vice versa. Then with the assistance of the energy (high temperature and pressure) in the hydrothermal reaction, BiOBr crystal could nucleate and grow on templates.

![Schematic diagram of the reaction process of BiOBr nanosheets.](image)

Figure 6.11 The schematic diagram of the reaction process of BiOBr nanosheets.
In this process, BiOBr single crystal seed should take a tetragonal shape (square shape) to maximize the expression of {001} facets and minimize the total surface energy according to Wulff theorem, because {001} facets have the lowest surface energy than other facets.[30-32] When the reaction speed is quick (high concentration of OH\(^-\) anions), as observed in TEM images, square nanosheets (BiOBr-square) can be harvested, accompanying with large inner strain in BiOBr crystal. However, when the reaction speed is slow (small concentration of OH\(^-\) anions), the shape of BiOBr nanosheets change to circle (BiOBr-circle), because in stress-free and initially defect-free nanocrystalline materials edge relaxations and reorientations are effective ways to release the inner strain. Therefore, even though the BiOBr nanosheets in two pH values both have a layer structure with same crystal structure and exposed facets, but with different growing speeds of the crystal, we could obtain BiOBr nanosheets with different degrees of inner strain. Moreover, relieving the inner strain by relaxation near the edge could create a lateral pseudo-heterostructure between the central and edge area in BiOBr-circle nanosheets.

### 6.5 Electronic properties characterization

The local electronic structures in 2D materials can be significantly affected by local strain.[33,34] To characterize to effect of the pseudo-heterointerface on the local electronic properties, we carried out the KPFM measurement, which can simultaneously acquire the surface morphologies and local work functions of BiOBr nanosheets.
Figure 6.12 (a) AFM image of BiOBr-square. (b) KPFM image of BiOBr-square. (c) Corresponding line profiles of the lines in a and b, with the height as a black line and the work function as a red line. (d) AFM image of BiOBr-circle. (e) KPFM image of BiOBr-circle. (f) The corresponding line profiles of the lines in d and e, with the height as a black line and work function as a red line.

As shown in Figure 6.12 (a) and (d), both square and circle BiOBr nanosheets present a flat surface. The morphologies are consistent with TEM results. Figure 6.12 (b) and (e) show the local work function mapping images acquired simultaneously with AFM measurements on square and circle BiOBr nanosheets, respectively. By measuring the CPD between the conductive tip with a constant work function and the surface, KPFM can precisely determine the work function of materials with high resolution.\[35\] The BiOBr-square nanosheet shows a homogeneous work function distribution across its entire surface, as demonstrated by the line profiles in Figure 6.12 (c). In contrast, the work function on the BiOBr-circle nanosheet exhibits an apparent variation between the area near the edge and the central area, as shown in Figure 6.12 (e) and the line profile in Figure 6.12 (f). We conjecture that the variation in the work function might be attributable to distinct local electronic structures induced by the inhomogeneous
distribution of local strains beside the lateral pseudo-heterointerface in BiOBr-circle nanosheets. This was also observed in the BiOBr nanosheets with intermediate shapes, as shown in Figure 6.13.

Figure 6.13 (a) The AFM image of the BiOBr-circle nanosheet with the shape between square and circle. (b) The corresponding KPFM image of the BiOBr nanosheet with only the circle area (indicated by green arrows) showing anisotropic charge distribution. Scale bars are 1 μm.

In order to verify this hypothesis, confocal Raman spectroscopy was employed (incident laser wavelength λ = 532 nm) to identify the correlation between the work function and the local strain in BiOBr nanosheets, as shown in Figure 6.14. Two strong phonon modes can be observed in the Raman spectra of the BiOBr samples. The Raman peaks of BiOBr-square are located at 118.3 cm⁻¹ and 160.5 cm⁻¹, while the Raman peaks of BiOBr-circle are located at 113.6 cm⁻¹ and 160.5 cm⁻¹. According to previous reports, the peak around 113.6 cm⁻¹ can be assigned to the A₁g mode (internal Bi-Br stretching), and the peak at 160.5 cm⁻¹ can be assigned to the E_g mode (internal Bi-Br stretching).[36] Although the E_g mode remains at 160.5 cm⁻¹ for both samples, the A₁g peak of BiOBr-square possesses a blue shift of ~5 cm⁻¹ from 113.6 cm⁻¹ to 118.3 cm⁻¹, which suggests a large inner compressive strain. Raman mapping of the A₁g peak on
both square and circle nanosheets were carried out to provide a straightforward way to identify the strain distributions. As shown in the insets in Figure 6.14, the intensity of the peak at 118.3 cm\(^{-1}\) for BiOBr-square was homogenously recorded across the whole nanosheet, indicating the homogeneous distribution of strain. In contrast, for BiOBr-circle, the intensity of the peak at 113.6 cm\(^{-1}\) is much stronger near the edge area than in the central area.

![Raman Spectra of BiOBr Nanosheets](image)

Figure 6.14 Raman spectra of BiOBr nanosheets, with BiOBr-square shown by the black line and BiOBr-circle by the red line. Insets are the Raman mappings at 118.3 cm\(^{-1}\) of BiOBr-square (top) and 113.6 cm\(^{-1}\) of BiOBr-circle (bottom).

This observation is supported by the fact that the relaxation of strain sprang from the edge area to the inner central area in BiOBr-circle nanosheets. It should be notice that during the Raman mapping, the resolution of is limited by the size of the laser spot,
which is around 361 nm in this work. The spatial variation in the \(A_{1g}\) peak is on a smaller scale than the resolution of the instrument, and so there is some averaging between each analysis spot, which will border the Raman activate area in the measurement. These results demonstrate that the variation of the local electronic structure can be directly correlated with its inhomogeneous strain distribution beside the lateral pseudo-heterointerface in the BiOBr-circle nanosheet.

### 6.6 DFT calculation of the strain effect on the band structure of BiOBr

We carried out DFT calculations to simulate the strain dependence of the electronic structure in BiOBr. Figure 6.15 (a) and (b) show DFT calculation results for the pristine and strain-applied BiOBr. When an in-plane strain (for example, the compressive strain here) is applied, the band structure and DOS of BiOBr are significantly modulated. The band gap is decreased by 0.2 eV in BiOBr under compressive strain (2.12 eV for pristine BiOBr). The CBM shifts from the Z point to the M point in the irreducible Brillouin zone, and the VBM moves from its position between the R and Z points to a position between the Z and A points. The most attractive feature in the electronic structure is that the band structure around the CBM is more dispersive in strained BiOBr than in pristine BiOBr. This suggests that the excited electrons in strained BiOBr have a small effective mass and high mobility. As a result, the total DOS of BiOBr can also be tuned by strain, as shown in Figure 6.15 (b), in which the partial DOS contributed by the O 2\(p\) orbitals is significantly changed. The change in the electronic structure can be ascribed to the symmetry transition in the BiOBr crystal under strain, which is a common phenomenon in many other semiconductors.\[37\] The DFT calculations indicate that the distinct electronic properties flanking the pseudo-
heterointerface in the BiOBr-circle nanosheets are indeed controlled by the local strain distribution, which supports our experimental findings.

Figure 6.15 (a) Calculated band structure of BiOBr, with the pristine BiOBr shown by the black solid line and the BiOBr with compressive strain shown by the red dashed line. (b) Calculated DOS of BiOBr, with the pristine BiOBr shown by the solid line and BiOBr with compressive strain shown by the dashed line.

The quantitative evaluation of strain effect on the electronic structures of BiOBr were estimated based on the DFT calculations. As shown in Figure 6.16, the value of $E_g$ of BiOBr, which determines its ability of light absorption and photoresponse threshold, varies remarkably under both compressive strain and tensile strain (vary from 1.27 eV to 2.67 eV). Meanwhile, the effect mass of charge carries near the CBM and VBM also exhibit strain-sensitive properties, according the result of DFT calculations, which will greatly affect the transport properties of charge carriers. The strain-sensitive electronic structure of BiOBr provides diversity in designing and creating heterostructures through strain engineering.
Figure 6.16 (a) The $E_g$ values of BiOBr under different degree of strain. (b) The effect mass of the electron at CBM and hole at VBM under different degree of strain, which is calculated from the second order of derivative of energy with respect to wave-vector.

6.7 Performance of BiOBr nanosheets in photoelectronic devices

Figure 6.17 (a) Photocurrent of individual BiOBr nanosheets. (b) Acquiring rise and decay time of BiOBr-square by fitting the on/off curve, inset is an image of the nanodevice. (c) Acquiring rise and decay time of BiOBr-circle by fitting the on/off curve, inset is the image of the device.

To verify the ability of separating photoexcited charge carriers in BiOBr nanosheets, photodetectors were fabricated on BiOBr-square and BiOBr-circle nanosheets, respectively, via electron-beam lithography. We measured the photocurrent and photoresponse of both BiOBr nanosheets. As shown in Figure 6.16 (a), under visible light irradiation (450 nm, 50 mW·cm$^{-2}$), photocurrent was generated in both BiOBr-square and BiOBr-circle nanosheets. The photocurrent generated in the BiOBr-circle
nanosheet is about 2 nA, which is nearly one order of magnitude larger than that of the BiOBr-square nanosheet under the same experimental conditions.

In addition to the contrasting photocurrents in these two BiOBr nanosheets, a difference in the photoresponse between BiOBr-square and BiOBr-circle nanosheets can be observed. Generally, the dynamic response of the rise (Equation 6.3) and decay (Equations 6.4 and 6.5) of photocurrent in BiOBr nanosheets can be fitted by the following stretched exponential functions:

\[ I = I_0 - I_0 e^{\frac{t}{\tau_r \gamma}} \]  
(6.3)

\[ I = I_0 e^{\frac{t}{\tau_d \gamma}} \]  
(6.4)

\[ I = A I_0 e^{\frac{t}{\tau_d \gamma}} + B I_0 e^{\frac{t}{\tau_d \gamma'}} \]  
(6.5)

where \(\tau_r\) and \(\tau_d\) are the relaxation time constants of the rise and decay, respectively. The parameter \(\gamma\) falls into the range of 0 to 1. As \(\gamma\) approaches 1, the function approaches classic single-exponential behavior without stretching. We have fitted the photoresponse curves of the BiOBr nanosheets to reveal the dynamic responses under visible light irradiation. As shown in Figure 6.17 (b), the \(\tau_r\) for BiOBr-square is calculated to be 0.24 s. The value of \(\gamma\) is calculated as 1, which suggests that the generation of photocurrent in BiOBr-square under light irradiation is dominated by the separation of photoexcited electron-hole pairs. The decay of photocurrent for BiOBr-square can be described by a stretched exponential function (Equation 6.4), where the value of \(\tau_d\) is 0.22 s and the value of \(\gamma\) is 0.16, suggesting that the recombination of photocurrent involves multiple energy processes, which may origin from the strain-induced distortion of the crystal lattice. For BiOBr-circle, as shown in Figure 6.17 (c), the rise of photocurrent could also be described using single exponential functions with \(\tau_r\) of 0.23 s, which is almost the same as for BiOBr-square. To describe the decay of
photocurrent in BiOBr-circle, however, at least two components are necessary to fit the persistent photocurrent decay, where two exponential functions (Equation 6.5) are used to separately analyze two different photo-relaxation processes. The $\tau_d$ of the fast process was determined to be 0.12 s with $\gamma$ as 0.29, and the $\tau'_d$ of the slow process was calculated to be 0.72 s with $\gamma$ as 0.05. During the photocurrent decay, it is well known that photoexcited electron-hole recombination dominates the fast decay process in the photocurrent. Hence, the photocurrent decreases very rapidly in the initial stage. The slow process is caused by a mechanism in which the photoexcited carriers are trapped and spatially separated by local potential fluctuations, which can suppress the electron-hole recombination. For our samples, because both the BiOBr-square and BiOBr-circle nanosheets exhibit defect-free characteristics, supported by the homogeneous element distribution across the whole nanosheets. Therefore, it is believed that the slow relaxation process in BiOBr-circle, which reflects the longer lifetime of photoexcited charge carriers, is governed by the strain-induced pseudo-heterointerface.

The responsivity ($R_\lambda$, Equation 6.6), and the external quantum efficiency (EQE, Equation 5.7) are two important measures for photoconductors and photodiodes.

$$R_\lambda = \frac{I_\lambda}{P_\lambda \times S} \quad (6.6)$$

$$EQE = \frac{h \pi R_\lambda}{\varepsilon \lambda} \quad (6.7)$$

where $I_\lambda$, represents the photocurrent ($I_{\text{illumination}} - I_{\text{dark}}$), $P_\lambda$ is the light intensity, $S$ is the effective device area under illumination, and $\lambda$, $h$, $c$, and $e$ are the wavelength of incident light, the Planck constant, the speed of light, and the charge of the electron, respectively. Based on photocurrent results, the values of $R_\lambda$ are 0.28 A/W and 1.29 A/W for BiOBr-square and BiOBr-circle, respectively. The corresponding EQE are, therefore, calculated as $0.77 \times 10^2$ % and $3.56 \times 10^2$ % (all parameters listed in Table 6.1), for BiOBr-square and BiOBr-circle, respectively.
Table 6.1 Calculated $R_{\lambda}$ and EQE for BiOBr nanosheets.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda$ (nm)</th>
<th>$P_{\lambda}$ (mW·cm$^{-2}$)</th>
<th>$I_{\lambda}$ (nA)</th>
<th>$S$ ($\mu$m$^2$)</th>
<th>$R_{\lambda}$ (A/W)</th>
<th>EQE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiOBr-square</td>
<td>450</td>
<td>50</td>
<td>0.26</td>
<td>1.83</td>
<td>0.28</td>
<td>$0.77 \times 10^2$</td>
</tr>
<tr>
<td>BiOBr-circle</td>
<td>450</td>
<td>50</td>
<td>1.80</td>
<td>2.80</td>
<td>1.29</td>
<td>$3.56 \times 10^2$</td>
</tr>
</tbody>
</table>

Figure 6.18 Schematic diagram of the band alignment at the pseudo-heterointerface in BiOBr-circle, which promotes the separation of photoexcited carriers.

We attribute the significant enhancement of the photocurrent in the BiOBr-circle nanosheets to improved separation efficiency of photoexcited charge carriers, which is illustrated in Figure 6.18. In the BiOBr-circle nanosheets, the inhomogeneous work function ($\phi$) distribution beside the lateral pseudo-heterointerface induces band bending across the interface.$^{[38]}$ Therefore, under light irradiation, photoexcited electrons and holes will be spatially driven by this electric field and separate to two different regions in the nanosheet, which will prolong their lifetime and consequently
enhance the light harvesting efficiency in the BiOBr-circle nanosheets. In contrast, there are not any pseudo-heterointerface in BiOBr-square nanosheets. Therefore, we do not expect the same scenario occurring in square nanosheets.

6.8 Summary

To summarize, the lateral pseudo-heterostructure on individual BiOBr nanosheets was fabricated by strain engineering. The local strain distribution has been revealed by TEM and Raman mapping. The dependence of local strain on electronic structures has been revealed by DFT calculations. An inhomogeneous work function distribution is observed across the lateral pseudo-heterostructure, which favors the separation of photoexcited charge carriers under visible light irradiation. Enhanced photocurrent (by one order of magnitude) has been achieved in BiOBr pseudo-heterostructure-based photodetectors, which is attributed to the appropriate band alignment across the pseudo-heterointerface. The growth of such lateral pseudo-heterostructures, thus, offers a promising way to build systems that show the functionalities of 2D lateral heterostructures but overcome the problems of lattice mismatch.

6.9 References


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Chapter 7 Summary and outlooks

OV defects were carefully introduced into rutile(110) single crystal by annealing in vacuum conditions in the temperature range from 900 K to 1300 K, which were checked by in-situ LT-STM. Isolated OV point defects were found on the rutile(110) (1×1) surfaces, which are favorable to be occupied by water molecule or OH. At 1300 K, the surface experienced the evolution from (1×2) to (1×2) surfaces, which were dominated by cross-links defects.

In further work, we demonstrate that inactive pure TiO$_2$ rutile(110) single crystal can be activated towards the HER by creating OV point defects. OVs and Ti$^{3+}$ ions in the surface region dominate the electrical conductivity of reduced TiO$_2$ and the amount of electrocatalytic active sites. Combining the well-characterized atomic surface structure and theoretical calculations, we conclude that subOVs can promote the electron transfer and hydrogen desorption in the electrocatalytic HER on reduced TiO$_2$ in alkaline media. It helps to elucidate the fundamental mechanism of the electrocatalytic activity of reduced oxides towards the HER, which is of immense fundamental and practical importance towards an in-depth understanding and rational optimization of TMOs as electrocatalysts in alkaline media. Considering that all the electrocatalytic characterization of TiO$_2$ were measured using the single crystals, which could benefit in controlling defect species and studying their roles in electrocatalytic reactions, synthesis TiO$_2$ materials in nano-scale will largely enhance the number of surface active sites and improve their performances. In addition, TiO$_2$(110) surface with (1×2) reconstruction has a complicated surface structure and cross-links defects, which could alter the surface electrocatalytic properties and electrical conductivity, providing an opportunity to further tune and enhance the electrocatalytic activities of TiO$_2$. 

137
Another focus was by the mean of precisely tuning the growth conditions, the strain can be controllably introduced into 2D BiOBr nanosheets with highly reactive [001] facets exposed. It is found that the strain effect can effectively tune the photocatalytic activity of BiOBr nanosheets in dye degradation. Our work suggests that strain engineering could be an effective approach to controlling the electronic structure of semiconductors for further enhancement of their efficiency in converting light into other forms of energy.

By characterizing single nanosheets with STEM, lateral pseudo-heterostructure was confirmed in BiOBr-circle nanosheets. The local strain distribution has been revealed by STEM and GPA analysis. The dependence of local strain on electronic structures has been revealed by DFT calculations. An inhomogeneous work function distribution is observed across the lateral pseudo-heterostructure, which favors the separation of photoexcited charge carriers under visible light irradiation. Enhanced photocurrent (by one order of magnitude) has been achieved in BiOBr pseudo-heterostructure-based photodetectors, which is attributed to the appropriate band alignment across the pseudo-heterointerface. The growth of such lateral pseudo-heterostructures, thus, offers a promising way to build systems that show the functionalities of 2D lateral heterostructures but overcome the problems of lattice mismatch.
Appendix A: List of publications


Appendix B: Conference contributions


