Doctoral Thesis in Chemistry

(Photo)electrochemical Water Oxidation: From Catalysis to Functional Device

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(Photo)electrochemical Water Oxidation: From Catalysis to Functional Device

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Academic Dissertation which, with due permission of the KTH Royal Institute of Technology, is submitted for public defence for the Degree of Doctor of Philosophy on Tuesday the 16th January 2024, at 10:00 a.m. in F3, Lindstedtsvägen 26, Stockholm.
The bad news is that we have still a long way to go.
The good news is that we have still a long way to go.
Hao Yang, 2024: “(Photo)electrochemical Water Oxidation: From Catalysis to Functional Device”, Department of Chemistry, School of Chemistry, Biotechnology and Health, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden.

**Abstract**

The key challenge within artificial photosynthesis is achieving efficient electro- or photo-driven water oxidation catalysis, a necessary process to supply the protons for the reduction reactions, thereby enabling solar fuel production. To facilitate efficient water (photo)electrolysis for solar fuel production, this thesis focuses on two aspects: 1) elucidating the O-O bond formation mechanism and developing efficient, stable, and economical water oxidation catalysts (WOCs); 2) exploring stable, low-cost, light-absorbing photoanode materials that have suitable band structures and excellent charge diffusion properties.

Chapter 1 provides an overview of the development of homogeneous and heterogeneous WOCs, with a particular emphasis on the catalytic mechanisms. Subsequently, it introduces the advancements in light-harvesting materials for photoelectrochemical cells and highlights the progress in the burgeoning field of lead halide perovskite-based photoanodes.

Chapter 2 clarifies the physical and electrochemical characterization methodologies, along with the protocols employed for mechanistic investigations in this thesis.

Chapter 3 introduces a host-guest complex, self-assembled through Co$^{2+}$ and cucurbit[5]uril (CB[5]), as a supramolecular WOC. This catalyst, Co@CB[5], was immobilized on indium tin oxide substrate and BiVO$_4$ photoanode for electrochemical and photoelectrochemical water oxidation. The role of Co@CB[5] in interfacial charge transfer is investigated by spectroscopic and electrochemical studies.

Chapter 4 reports a molecularly well-defined heterogeneous WOC with aza-fused, π-conjugated microporous polymer coordinated single cobalt sites (AzaCMP-Co). Integrating experimental and theoretical results, this work highlights the significance of electrolyte pH and the role of regulating the intramolecular hydroxyl nucleophilic attack pathway in enhancing water oxidation activity.

Chapter 5 presents a stable formamidinium lead bromide (FAPbBr$_3$) photoanode for water oxidation to achieve an exceptionally low onset potential. Theoretical calculations and spectroscopic characterizations reveal the origin
of low onset potential, which offers pivotal insights in guiding the development of photovoltaic material-based photoelectrodes for solar fuel applications.

**Keywords:** artificial photosynthesis, solar fuels, water oxidation, nucleophilic attack, conjugated microporous polymer, host-guest chemistry, photoanode, perovskites
Sammanfattning på Svenska

Den huvudsakliga utmaningen inom artificiell fotosyntes är att uppnå effektiv elektro- eller fotodriven vattenoxidationskatalys, en nödvändig process för att tillhandahålla protoner för reduktionsreaktioner, vilket möjliggör produktion av solbränsle. För att underlätta effektiv vatten(foto)elektrolys för produktion av solbränsle fokuserar denna avhandling på två aspekter: 1) klargörande av O-O-bindningens bildningsmekanism och utveckling av effektiva, stabila och ekonomiska vattenoxidationskatalysatorer (WOCs); 2) utforskning av stabila, lågkostnads, ljusabsorberande fotoanodematerial som har lämpliga bandstrukturer och utmärkta egenskaper för laddningsdiffusion.

Kapitel 1 ger en översikt över utvecklingen av homogena och heterogena WOCs, med särskilt fokus på katalytiska mekanismer. Därefter introduceras framstegen inom ljusinsamlingsmaterial för fotoelektrokemiska celler och framstegen inom det växande området av blyhalid-perovskitbaserade fotoanoder lyfts fram.

Kapitel 2 klargör de fysiska och elektrokemiska karakteriseringssmetoderna, tillsammans med de protokoll som används för mekanismundersökningar i denna avhandling.

Kapitel 3 introducerar ett värd-gäst-komplex, självmonterat genom Co$^{2+}$ och cucurbit[5]uril (CB[5]), som en supramolekylär WOC. Denna katalysator, Co@CB[5], immobiliserades på substrat av indiumtennoxid och BiVO$_4$-fotoanoder för elektrokemisk och fotoelektrokemisk vattenoxidation. Rollen för Co@CB[5] i gränsskiktets laddningstransfer undersöks genom spektroskopisk och elektrokemiska studier.


Kapitel 5 presenterar en stabil fotoanod av formamidinium blybromid (FAPbBr$_3$) för vattenoxidation för att uppnå en exceptionellt låg startpotential. Teoretiska beräkningar och spektroskopisk karakteriseringer avslöjar ursprunget till den låga startpotentialen, vilket ger avgörande insikter för den fortsatta utvecklingen av fotovoltaiska materialbaserade fotoelektroder för solbränsletillämpningar.
Nyckelord: artificiell fotosyntes, solbränslen, vattenoxidation, nukleofil attack, konjugerad mikroporös polymer, värd-gästkemi, fotoanoder, perovskiter
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>Electrode area</td>
</tr>
<tr>
<td>a</td>
<td>Activity of the reactant in solution</td>
</tr>
<tr>
<td>ABPE</td>
<td>Applied bias photon-to-current efficiency</td>
</tr>
<tr>
<td>acac</td>
<td>Acetylacetone</td>
</tr>
<tr>
<td>AEM</td>
<td>Adsorbate evolution mechanism</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>APT</td>
<td>Atom-proton transfer</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflectance</td>
</tr>
<tr>
<td>Aza-CMP</td>
<td>Aza-fused π-conjugated microporous polymer</td>
</tr>
<tr>
<td>BHC</td>
<td>Bimolecular hydroxyl coupling</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction band</td>
</tr>
<tr>
<td>CB[n]</td>
<td>Cucurbit[n]uril</td>
</tr>
<tr>
<td>CBM</td>
<td>Conduction band minimum</td>
</tr>
<tr>
<td>COF</td>
<td>Covalent organic framework</td>
</tr>
<tr>
<td>CP</td>
<td>Carbon paper</td>
</tr>
<tr>
<td>CPET</td>
<td>Concerted proton-coupled electron transfer</td>
</tr>
<tr>
<td>CP-MAS</td>
<td>Cross-polarization magic angle spinning</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>E</td>
<td>Applied potential</td>
</tr>
<tr>
<td>$E^0$</td>
<td>Formal redox potential</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation energy at the equilibrium potential</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraacetate</td>
</tr>
<tr>
<td>$E_F$</td>
<td>Fermi level</td>
</tr>
<tr>
<td>$E_{fb}$</td>
<td>Flat-band potential</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>$E_{OER}$</td>
<td>Thermodynamic potential required for water oxidation</td>
</tr>
<tr>
<td>$E_{onset}$</td>
<td>Onset potential</td>
</tr>
<tr>
<td>$E_p$</td>
<td>Peak potential of M$^{n+}$ oxidation reaction</td>
</tr>
<tr>
<td>$E_r$</td>
<td>Peak potential of M$^{(n+1)+}$ oxidation reaction</td>
</tr>
<tr>
<td>$E_{read}$</td>
<td>Potential read by the reference electrode</td>
</tr>
<tr>
<td>ET</td>
<td>Electron transfer</td>
</tr>
<tr>
<td>ETL</td>
<td>Electron transport layer</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray absorption fine structure</td>
</tr>
<tr>
<td>F</td>
<td>Faraday constant</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>VI</td>
<td>CH(NH₂)₂⁺</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>FOWA</td>
<td>Foot of the wave analysis</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine doped tin oxide</td>
</tr>
<tr>
<td>GS</td>
<td>Graphite sheet</td>
</tr>
<tr>
<td>h</td>
<td>Planck constant</td>
</tr>
<tr>
<td>ℏ</td>
<td>Reduced Planck constant</td>
</tr>
<tr>
<td>HAADF</td>
<td>High-angle annular dark-field</td>
</tr>
<tr>
<td>HER</td>
<td>Hydrogen evolution reaction</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High-resolution transmission electron microscopy</td>
</tr>
<tr>
<td>HTL</td>
<td>Hole transport layer</td>
</tr>
<tr>
<td>HTM</td>
<td>Hole transport material</td>
</tr>
<tr>
<td>I₂M</td>
<td>Interaction of two metal-oxos</td>
</tr>
<tr>
<td>i-APT</td>
<td>Intramolecular atom-proton transfer</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively coupled plasma-optical emission spectroscopy</td>
</tr>
<tr>
<td>IHC</td>
<td>Intramolecular hydroxyl coupling</td>
</tr>
<tr>
<td>IHNA</td>
<td>Intramolecular hydroxyl nucleophilic attack</td>
</tr>
<tr>
<td>IHP</td>
<td>Inner Helmholtz plane</td>
</tr>
<tr>
<td>i-I₂M</td>
<td>Intramolecular interaction of two metal-oxos</td>
</tr>
<tr>
<td>iₖ</td>
<td>Kinetic current</td>
</tr>
<tr>
<td>IMPS</td>
<td>Intensity modulated photocurrent spectroscopy</td>
</tr>
<tr>
<td>IOC</td>
<td>Intermolecular oxo/oxyl coupling</td>
</tr>
<tr>
<td>IPCE</td>
<td>Incident photon-to-current efficiency</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>j</td>
<td>Current density</td>
</tr>
<tr>
<td>j_{dark}</td>
<td>Dark current</td>
</tr>
<tr>
<td>j_{light}</td>
<td>Photocurrent</td>
</tr>
<tr>
<td>J_{op}</td>
<td>Operational current density</td>
</tr>
<tr>
<td>J_{ph}</td>
<td>Photocurrent density</td>
</tr>
<tr>
<td>J_{sc}</td>
<td>Short circuit current</td>
</tr>
<tr>
<td>k₀</td>
<td>Standard rate constant</td>
</tr>
<tr>
<td>Kₐ</td>
<td>Acid dissociation constant</td>
</tr>
<tr>
<td>k_{ap}</td>
<td>Apparent rate constant</td>
</tr>
<tr>
<td>kₐ</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>k_{ET}</td>
<td>Rate constant of the electron transfer process</td>
</tr>
<tr>
<td>KIEs</td>
<td>Kinetic isotope effects</td>
</tr>
<tr>
<td>k_{PCET}</td>
<td>Rate constant of the proton-coupled electron transfer process</td>
</tr>
<tr>
<td>k_{PT}</td>
<td>Rate constant of the proton transfer process</td>
</tr>
</tbody>
</table>
\[ k_{\text{rec}} \] Rate constants of charge recombination
\[ k_{\text{trans}} \] Rate constants of interfacial charge transfer
\[ k_w \] Ionic product of water
LDH Layered double hydroxide
LOM Lattice oxygen mechanism
\[ L_p \] Minority carrier diffusion length
LSV Linear sweep voltammetry
MA \( \text{CH}_3\text{NH}_3^+ \)
M-COF Metalated COF
MHP Metal halide perovskite
MOF Metal organic framework
\[ N_D \] Donor density
\[ nE_F \] Quasi-Fermi level for electrons
NHE Normal hydrogen electrode
NLDFT Non-local density functional theory
NMR Nuclear magnetic resonance
OCM Oxygen coupling mechanism
OEC Oxygen evolution complex
OER Oxygen evolution reaction
OHP Outer Helmholtz plane
PCE Power conversion efficiency
PCET Proton-coupled electron transfer
PEC Photoelectrochemical
\[ pE_F \] Quasi-Fermi level for holes
\[ P_{\text{light}} \] Intensity of incident light
PSII Photosystem II
PT Proton transfer
PV Photovoltaic
PV-EC Photovoltaic-electrolyzer
PVM-PEC PV materials-based photoelectrochemical cell
\[ P_\lambda \] The light intensity at each wavelength
QFLS Quasi-Fermi level splitting
R Universal gas constant
\[ R_{\text{ct}} \] Charge-transfer resistance
RDS Rate-determining step
RHE Reversible hydrogen electrode
RI Redox isomerization
SAC Single-atom catalyst
SDG Sustainable development goal
SEM Scanning electron microscope
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>STM</td>
<td>Scanning tunnelling microscopy</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>TCO</td>
<td>Transparent conducting oxide</td>
</tr>
<tr>
<td>TDOS</td>
<td>Total density of states</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TOF</td>
<td>Turnover frequency</td>
</tr>
<tr>
<td>TON</td>
<td>Turnover number</td>
</tr>
<tr>
<td>UPS</td>
<td>Ultraviolet photoelectron spectroscopy</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>ν</td>
<td>Scan rates</td>
</tr>
<tr>
<td>VB</td>
<td>Valence band</td>
</tr>
<tr>
<td>VBM</td>
<td>Valence band maximum</td>
</tr>
<tr>
<td>$V_{oc}$</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>$V_{ph}$</td>
<td>Photovoltage</td>
</tr>
<tr>
<td>$W$</td>
<td>Activation energy at a specific overpotential</td>
</tr>
<tr>
<td>WNA</td>
<td>Water nucleophilic attack</td>
</tr>
<tr>
<td>WOC</td>
<td>Water oxidation catalyst</td>
</tr>
<tr>
<td>WT</td>
<td>Wavelet transform</td>
</tr>
<tr>
<td>XANES</td>
<td>X-ray absorption near edge structure</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray absorption spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Transfer coefficient</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>Amount of surface metal centers</td>
</tr>
<tr>
<td>$\Delta G$</td>
<td>Gibbs energy change</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Overpotential</td>
</tr>
<tr>
<td>$\eta_{bulk}$</td>
<td>Inner charge separation and transport efficiency</td>
</tr>
<tr>
<td>$\eta_F$</td>
<td>Faradaic efficiency</td>
</tr>
<tr>
<td>$\eta_{STH}$</td>
<td>Solar-to-hydrogen conversion efficiency</td>
</tr>
<tr>
<td>$\eta_{surface}$</td>
<td>Interfacial carrier injection efficiency</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Reorganization energy</td>
</tr>
</tbody>
</table>
List of Publications

This thesis is based on the following papers, referred to in the text by their Roman numerals I-III:

I. **A Cobalt@Cucurbit[5]uril Complex as a Highly Efficient Supramolecular Catalyst for Electrochemical and Photoelectrochemical Water Splitting**
   Fusheng Li,† Hao Yang,† Qiming Zhuo, Dinghua Zhou, Xiujuan Wu, PeiLi Zhang, Zhaoyang Yao, Licheng Sun († authors contributed equally to this work)

II. **Intramolecular Hydroxyl Nucleophilic Attack Pathway by a Polymeric Water Oxidation Catalyst with Single Cobalt Sites**
    Hao Yang, Fusheng Li, Shaoqi Zhan, Yawen Liu, Wenlong Li, Qijun Meng, Alexander Kravchenko, Tianqi Liu, Yi Yang, Yuan Fang, Linqin Wang, Jiaqi Guan, István Furó, Mårten S. G. Ahlquist, Licheng Sun

III. **Monolithic FAPbBr₃ Photoanode for Photoelectrochemical Water Oxidation with Low Onset-potential and Enhanced Stability**
    Hao Yang, Yawen Liu, Yunxuan Ding, Fusheng Li, Linqin Wang, Bin Cai, Fuguo Zhang, Tianqi Liu, Gerrit Boschloo, Erik M. J. Johansson, Licheng Sun
Papers not included in this thesis:

IV. **Intramolecular Proton Transfer Boosted O-O Bond Formation on Molecular Ni-Fe Sites**
Hao Yang, Fusheng Li, Shaoqi Zhan, Yawen Liu, Linqin Wang, Wenlong Li, Tianqi Liu, Erik M. J. Johansson, Mårten S. G. Ahlquist, and Licheng Sun
*Manuscript.*

V. **Dynamic Active Site Formation Triggered Sequential Proton-Electron Transfer for Highly Efficient Water Oxidation Catalysis**
Hao Yang, Fusheng Li, Zhen Qiu, Wenlong Li, Chang Liu, Xiujuan Wu, PeiLi Zhang, Tomas Edvinsson, Yu Shan and Licheng Sun
*Manuscript.*

VI. **Integrating Cobalt-sites-rich Aza-fused Conjugated Microporous Polymers on BiVO₄ for Efficient Photoelectrochemical Water Splitting**
Qijun Meng, Hao Yang, Ying Gao, Yingzheng Li, Alexander Kravchenko, Qinglu Liu, Yi Yang, Yawen Liu, Yu Shan, Fusheng Li and Licheng Sun
*Manuscript.*

VII. **Solvent Engineering of Perovskite Crystallization for High Band Gap FAPbBr₃ Perovskite Solar Cells Prepared in Ambient Condition**
Yawen Liu, Bin Cai, Hao Yang, Gerrit Boschloo, Erik M. J. Johansson

VIII. **Bioinspired Active Site with a Coordination-Adaptive Organosulfonate Ligand for Catalytic Water Oxidation at Neutral pH**
Tianqi Liu, Shaoqi Zhan, Nannan Shen, Linqin Wang, Zoltán Szabó, Hao Yang, Mårten S. G. Ahlquist, Licheng Sun

IX. **2D Materials for Solar Fuels via Artificial Photosynthesis**
Jian Du, Hao Yang, Licheng Sun
X. A Phenanthrocarbazole-Based Dopant-Free Hole-Transport Polymer with Noncovalent Conformational Locking for Efficient Perovskite Solar Cells
Yaxiao Guo, Lanlan He, Jiaxin Guo, Yu Guo, Fuguo Zhang, Linqin Wang, Hao Yang, Chenhao Xiao, Yi Liu, Yongsheng Chen, Zhaoyang Yao, Licheng Sun

XI. Promoting Proton Transfer and Stabilizing Intermediates in Catalytic Water Oxidation via Hydrophobic Outer Sphere Interactions
Tianqi Liu, Ge Li, Nannan Shen, Linqin Wang, Brian J. J. Timmer, Alexander Kravchenko, Shengyang Zhou, Ying Gao, Yi Yang, Hao Yang, Bo Xu, Biaobiao Zhang, Mårten S. G. Ahlquist, Licheng Sun

XII. Promotion of the Oxygen Evolution Performance of Ni-Fe Layered Hydroxides via the Introduction of a Proton-Transfer Mediator Anion
Wenlong Li, Fusheng Li, Yilong Zhao, Chang Liu, Yingzheng Li, Hao Yang, Ke Fan, Peili Zhang, Yu Shan, Licheng Sun

XIII. Selective Electrochemical Alkaline Seawater Oxidation Catalyzed by Cobalt Carbonate Hydroxide Nanorod Arrays with Sequential Proton-Electron Transfer Properties
Gang Li, Fusheng Li, Yilong Zhao, Wenlong Li, Ziqi Zhao, Yingzheng Li, Hao Yang, Ke Fan, Peili Zhang, Licheng Sun

XIV. Remarkable Synergy of Borate and Interfacial Hole Transporter on BiVO4 Photoanodes for Photoelectrochemical Water Oxidation
Qijun Meng, Biaobiao Zhang, Hao Yang, Chang Liu, Yingzheng Li, Alexander Kravchenko, Xia Sheng, Lizhou Fan, Fusheng Li, Licheng Sun

XV. A Dendritic Sb2Se3/In2S3 Heterojunction Nanorod Array Photocathode Decorated with a MoSx Catalyst for Efficient Solar Hydrogen Evolution
Chang Liu, Tao Liu, Yingzheng Li, Ziqi Zhao, Dinghua Zhou, Wenlong Li, Yilong Zhao, Hao Yang, Licheng Sun, Fusheng Li, Zhiqiang Li
XVI. **Electrochemical and Photoelectrochemical Water Splitting with a CoO\textsubscript{x} Catalyst Prepared by Flame Assisted Deposition**

Fusheng Li, Ziqi Zhao, Hao Yang, Dinghua Zhou, Yilong Zhao, Yingzheng Li, Wenlong Li, Xiujuan Wu, Peili Zhang, Licheng Sun


XVII. **A Bio-Inspired Coordination Polymer as Outstanding Water Oxidation Catalyst via Second Coordination Sphere Engineering**

Wenlong Li, Fusheng Li, Hao Yang, Xiujuan Wu, Peili Zhang, Yu Shan, Licheng Sun

*Nat. Commun.*, 2019, 10, 5074.
Contributions to the Papers

**Paper I:** I performed all the material synthesis, most of the structural characterization, and the electrochemical measurements. I analyzed and interpreted most of the spectral and electrochemical kinetics data and assisted in revising the manuscript.

**Paper II:** I performed all the catalyst synthesis, most of the structural characterization, and the electrochemical measurements. I analyzed and interpreted most of the spectral and electrochemical kinetics data and wrote the original manuscript.

**Paper III:** I performed most of the synthesis, structural, and electrochemical characterizations. I contributed to the analysis and interpretation of the data and wrote the original manuscript.
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1. Introduction

From the first stirrings of life underwater to the great beasts of the Stone Age, to humans taking their first upright steps, we human beings have come far. Newly explored domains have broadened our horizons, and our relentless pursuit of energy propels the ceaseless advancement of science and culture. From the first fire by drilling wood to the constant hum of machinery, coal, emblematic of the first industrial revolution that began in Great Britain, ushered humanity into the era of industry. With the rise of aviation and new communication methods, our world has become increasingly connected and familiar. In the early 20th century, the utilization of the internal combustion engine brought petroleum to the spotlight of history. Due to its convenient transportation and high energy density, it emerged as the primary energy source for transportation. Furthermore, as the base material for many industrial chemicals, petroleum has established itself as one of the most pivotal commodities in the contemporary world.

Throughout history, with the continuous use of wood, charcoal, coal, petroleum, and natural gas, humanity's energy utilization has been intricately linked to the carbon cycle on Earth. As human society has evolved, the consumption of reduced carbon and the emission of oxidized carbon have become inevitable trends. During the agricultural era, carbon dioxide (CO$_2$) emissions and neutralization maintained a delicate balance. However, with the onset of the industrial age, this balance was disrupted by the extensive use of fossil fuels, including coal, petroleum, and natural gas (Figure 1a). In 1950, the world emitted 6 billion tons of CO$_2$. By 1990, this number had increased almost threefold, surpassing 22 billion tons. What is even more concerning is that CO$_2$ emissions are still rising rapidly, with our current annual emissions exceeding 35 billion tons. The connection between global temperatures and the concentration of greenhouse gases (especially CO$_2$) has been consistent throughout Earth's history. As presented in Figure 1b, global temperatures have risen sharply over the past few decades, about 1.0°C higher than the 1951-1980 baseline. The CO$_2$ and other greenhouse gases emitted by humans are the primary drivers of climate change and represent one of the most pressing challenges in the world today.

Climate change has become a focal point of global concern, prompting the creation of a series of significant international agreements and frameworks, such as the United Nations Framework Convention on Climate Change (UNFCCC), Kyoto Protocol, Paris Agreement, Copenhagen Accord, Cancún
Agreements, and the Katowice Rulebook. These initiatives strive to diminish greenhouse gas emissions, promote a transition to a low-carbon society, and strengthen nations' resilience against climate challenges. In this context, to effectively address the greenhouse effect and climate change, it is essential to enact a series of strategies and measures within the energy domain. This involves maximizing the energy efficiency of existing fossil fuels and undertaking the crucial and pressing transition to renewable energy sources.

1.1 Renewable energy perspective

The contemporary global energy composition comprises a variety of sources, including biomass, coal, oil, gas, nuclear, and diverse renewables, such as hydropower, solar, and wind. Since the inception of the industrial era, fossil fuels have held a central position in modern civilization. Throughout the 20th century, global energy sources diversified considerably (Figure 2a). While
oil and gas initially held dominance, hydropower soon joined the portfolio in the early 1900s. The 1960s heralded the incorporation of nuclear energy, while the 1980s introduced what is commonly termed "modern renewables," specifically solar and wind energy. As indicated in the recent Statistical Review of World Energy, fossil fuels still persist as the preeminent energy source utilized worldwide. By 2022, total global energy consumption exceeded 178 Tera Watt hour (TWh); an estimated 17% of global energy was derived from low-carbon mediums: nuclear contributed slightly above 4%, while the subsequent 13% was sourced from various renewable methodologies (Figure 2b).

![Figure 2. Global primary energy consumption by source. (a) Total consumption from 1960 to 2022. (b) The proportion of different sources of world energy consumption in 2022. Source data obtained from Energy Institute Statistical Review of World Energy (2023).](image)

In line with historical trends, the electricity sector continues to lead with a pronounced 29.9% share in renewable energy utilization (Figure 3a). Notwithstanding the perturbations induced by the COVID-19 pandemic and subsequent fluctuations in global commodity prices, which disrupted the renewable energy supply chain and postponed various projects, the electricity generated from renewable modalities experienced a record-breaking increase. In 2022, electricity generation based on renewable energy reached 8532.6

3
TWh, which is more than double that of 2010 (4180 TWh). Solar and wind provide more than 10% of the world's electricity for the first time as global electricity generation hits a record high. By the end of 2022, solar power generation accounted for 15.49% of renewable electricity production, representing a significant increase from the mere 2.16% observed a decade prior (Figure 3b).

![Figure 3](image)

**Figure 3.** (a) Electricity production from fossil fuels, nuclear and renewables. (b) The proportion of different sources in renewable electricity generation. Source data obtained from Energy Institute Statistical Review of World Energy (2023).

Historically, the cost of solar photovoltaic (PV) modules has shown an almost exponential decline with the increase in installed capacity (Figure 4a). By 2021, the price of these modules had decreased to a mere 0.27 USD/W, marking a tenfold reduction over the previous decade. Between 2010 and 2021, the balance of competitiveness between renewables and existing fossil fuels and nuclear power underwent a significant transformation. During this timeframe, the global weighted average levelised cost of electricity (LCOE)
for newly commissioned grid-scale solar PV projects plummeted by 88% (Figure 4b). Concurrently, the costs of onshore and offshore wind power witnessed reductions of 68% and 60%, respectively. In 2021, the global weighted average LCOE for new grid-scale solar PV and hydroelectric projects was 11% lower than that of the most cost-effective new fossil fuel-based plants. With ongoing enhancements in installed capacity, the cost benefits of PV power generation will become increasingly pronounced. By 2035 and 2050, the anticipated costs for new photovoltaic power generation are projected to decrease by approximately 50% and 70%, respectively, from present estimates, settling at approximately 0.03 USD/kWh and 0.02 USD/kWh.

Figure 4. (a) Solar PV panel prices vs. cumulative capacity. Source data obtained from references 5-7. (b) LCOE of newly commissioned utility-scale solar photovoltaic, onshore, and offshore wind. Source data obtained from reference 5.

As the adoption of PV and wind power is projected to surge in the forthcoming years, there is an escalating urgency for convenient, efficient, and cost-effective energy storage methods within the power sector. Both
wind and PV power outputs are significantly influenced by natural conditions, exhibiting intermittent, fluctuating, and uncertain characteristics. A considerable proportion of renewable energy can affect the stable operation of the power grid. Curtailment level serves as a crucial indicator of the impact of renewable energy on grid operations. Notably, the overall curtailment levels correlate positively with the penetration rate of renewable energy. Specifically, for every 1% rise in renewable energy penetration, the average curtailment level increment ranges from 0.02% to 2.97%. Consequently, addressing the consumption challenges posed by high renewable energy proportions in the power system and minimizing the curtailment level will become crucial.

Electrical energy storage is pivotal for addressing these challenges and facilitating up to 100% renewable energy integration into the grid. As identified in Beaudin's review, a storage capacity equating to 10-20% of the total intermittent renewable energy production is typically required for effective grid integration. In 2022, the worldwide energy storage capacity, which includes both electrochemical and electro-mechanical mechanisms, amounted to 194 GW. This is only approximately 10% of the aggregate installed capacity of solar PV and wind energy, with a sum of 1945.4 GW (1046.6 GW from solar PV, 835.6 GW via onshore wind, and 63.2 GW through offshore wind). The gap between energy storage and renewable energy capacities highlights the urgent demand for large-scale, long-term energy storage solutions, whether for seasonal backup or as energy security reserves in the substantial replacement of fossil fuels.

Electric energy can be transformed into various forms for storage, such as chemical, potential, kinetic, and electromagnetic energy. Based on specific techniques, this storage can be categorized into three primary types: mechanical, electromagnetic, and chemical energy storage. Mechanical energy storage encompasses pumped hydro, compressed air, and flywheel storage. Electromagnetic storage includes superconducting mechanisms, supercapacitors, and high-density capacitors. Meanwhile, electrochemical storage methods involve batteries (including lead acid, nickel-metal hydride, nickel-cadmium, lithium-ion, sodium-sulfur, and liquid flow batteries) and hydrogen storage. Of these, pumped hydro storage stands out as the predominant technology, accounting for 94.5% of the global grid-connected electricity storage capacity till 2022 (Figure 5b). While it holds potential for a sustainable energy future, its growth is constrained by factors like a scarcity of suitable locations, prolonged development times, high upfront capital requirements, and pronounced environmental consequences. The remaining 5.5% of the global grid-connected electricity storage capacity consists of
diverse technologies, primarily short-term storage options like batteries, flywheels, and capacitors. Among these, battery technology has demonstrated potential for commercial viability, especially with the rising adoption of residential solar PV. However, despite its prominence, battery storage presents challenges related to storage capacity and discharge duration (Figure 5a). When accounting for factors, such as equipment cost, maintenance, and transportation, battery technology may not emerge as the optimal solution for large-scale, long-term, and long-distance energy storage and distribution.

![Figure 5](image)

**Figure 5.** (a) Comparison of discharge time vs. capacity of energy storage technologies. Figure adapted from reference 13. (b) The proportion of different types of globally installed energy storage projects till 2022. Source data obtained from DOE Global Energy Storage Database.10

Hydrogen is regarded as an optimal energy carrier for storing and distributing renewable energies, given its impressive gravimetric energy density of approximately 140 MJ kg\(^{-1}\). This density surpasses that of many conventional fuels, such as gasoline (49 MJ kg\(^{-1}\)), diesel (34 MJ kg\(^{-1}\)), methane (44 MJ kg\(^{-1}\)), and methanol (20 MJ kg\(^{-1}\)).14,15 In terms of emerging long-term electrical storage solutions, hydrogen storage faces fewer constraints and can be
directly employed as a fuel for transportation, as well as in industrial and chemical operations. Hydrogen combustion produces no greenhouse gases. Furthermore, when hydrogen is derived from renewable energy sources like solar, it sidesteps the prevalent method of producing H₂ from fossil fuels, such as methane steam reforming and coal gasification. As a result, hydrogen maintains a low-carbon footprint from production to final use.

Hydrogen technology offers immense promise for large-scale, long-duration storage, essential for achieving ambitious renewable energy goals. The prospective energy framework will likely emphasize both immediate-use electricity and deferred-use hydrogen, working in tandem with other storage modalities. Rather than competing, these technologies will collectively bolster the energy security of a sustainable global society. As previously highlighted, renewable hydrogen technology holds immense promise in addressing energy challenges, seamlessly aligning with Sustainable Development Goal (SDG) 7, which advocates for affordable and clean energy for all. Its influence extends far beyond mere energy production. Energy is the backbone of many essential human activities; a sustainable approach to energy production and storage, such as solar fuel technology, can tangentially support the attainment of various SDGs. These encompass catalyzing Industry, Innovation, and Infrastructure (SDG 9) and cultivating Sustainable Cities and Communities (SDG 11). Equally compelling are the environmental merits of renewable hydrogen. By utilizing a clean energy source, greenhouse gas emissions should be substantially reduced, which is in line with Climate Action (SDG 13). Such reductions can cascade positive impacts on Life Below Water (SDG 14) and contribute to the Sustainable Consumption and Production Patterns (SDG 12). Additionally, as this technology does not rely on vast amounts of water, unlike some conventional power generation methods, it supports the Clean Water and Sanitation (SDG 6) goal and promotes Decent Work and Economic Growth (SDG 8) by potentially creating jobs in the renewable energy sector.

1.2 Solar fuels

Solar energy offers a virtually inexhaustible, clean, and sustainable power source. The daily solar irradiance on Earth is approximately 10^{22} joules; in a single hour, the sun provides Earth with more energy than what we consume from fossil fuels, nuclear power, and all other renewable sources combined over an entire year. According to projections from the International Energy Agency (IEA), by 2050, renewable energy is expected to constitute over 60% of the global energy supply, with solar energy emerging as the principal contributor, representing one-fifth of the total supply. Solar energy has great potential as a clean, cheap, renewable, and sustainable energy source,
but it must be captured and transformed into applicable forms of energy as plants do. As previously discussed, hydrogen, owing to its renewable and carbon-neutral characteristics, emerges as an exemplary green energy carrier with considerable energy density. Generating hydrogen through sustainable and carbon-neutral methods, such as water splitting electrolysis powered by renewable sources or artificial photosynthesis, represents an optimal strategy for advancing sustainable energy infrastructures.

The water splitting reaction (Equation 1) encompasses two half-reactions: i) water oxidation ($E^0 = 1.23$ V vs. reversible hydrogen electrode (RHE)), wherein two water molecules undergo oxidation to produce a single oxygen molecule, yielding four protons and four electrons (Equation 2), and ii) proton reduction ($E^0 = 0$ V vs. RHE), during which protons are reduced to yield hydrogen (Equation 3). The overall water splitting process is an energetically uphill reaction and necessitates a standard Gibbs free energy change ($\Delta G^0$) of 237.2 kJ mol$^{-1}$ at 298 K.$^{18}$

\[
\begin{align*}
\text{Overall water splitting:} & \quad \Delta G^0 = 237.2 \text{ kJ mol}^{-1}, \\
2 \text{H}_2\text{O} & \rightarrow \text{O}_2 + 2 \text{H}_2 \\
\Delta E^0 & = 1.23 \text{ V vs. RHE} \quad (1) \\
\text{Water oxidation:} & \\
2 \text{H}_2\text{O} & \rightarrow \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \quad E^0 = 1.23 \text{ V vs. RHE} \quad (2) \\
\text{Proton reduction:} & \\
2 \text{H}^+ + 2 \text{e}^- & \rightarrow \text{H}_2 \quad E^0 = 0 \text{ V vs. RHE} \quad (3)
\end{align*}
\]

This carbon-neutral chemical reaction requires merely sunlight or green electricity as the energy source and utilizes abundant raw materials, H$_2$O, yielding only O$_2$ as the byproduct. Additionally, the product of solar fuels is not confined to hydrogen alone. The protons and electrons derived from the water oxidation process can facilitate the conversion of other small molecules, such as carbon dioxide, nitrogen and biomass, into fuels or high-value chemical products (Equation 4).

\[
2 \text{H}_2\text{O} \xrightarrow{\text{Solar energy}} \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \quad (4)
\]

1.2.1 Photosynthesis: from natural to artificial

Natural photosynthesis converts CO$_2$ and H$_2$O into carbohydrates and O$_2$ using solar energy through photosystem II (PSII) and photosystem I (PSI).$^{19}$ Water oxidation at the oxygen evolution complex (OEC: Mn$_4$CaO$_5$) within PSII provides the protons and electrons for CO$_2$ reduction by Ribulose-1,5-
biphosphate carboxylate/oxygenase (RuBisCo). These protons and electrons are also directly or indirectly involved in other enzymatic reactions, such as hydrogen evolution by hydrogenases (H₂ase), nitrogen fixation by nitrogenase (N₂ase), and oxygen reduction by cytochrome c oxidase (CCO) (Figure 6). A comprehensive understanding of natural photosynthesis enables the replication of its functions in artificial photosynthesis systems, facilitating the conversion of solar energy and substrates into fuels and valuable chemical products.

**Figure 6.** Schematic representation of natural enzymes detailing their active site structures and roles as potential models for artificial photosynthesis. (a) RuBisCo, (b) H₂ase, (c) N₂ase, (d) CCO and (e) PSII in nature. Adapted with permission from reference 20. Copyright 2021, Oxford University Press.

The utilization of solar energy by the natural photosynthetic system includes three principal processes: light capture, charge separation, and reaction catalysis (Figure 7). In the electron transport chain of the natural photosynthetic system (known as the Z-scheme), light excites the P680 dye in photosystem II, leading to charge separation. Under the turnover of the OEC, the electrons extracted from water are injected into photosystem I with elevated energy. Within photosystem I, light further excites these electrons via the P700 dye, boosting them to an even higher energy state before their transfer to ferredoxin-NADP reductase (FNR) facilitates the conversion of NADP⁺ to NADPH. This electron transfer process creates a transmembrane proton concentration gradient, supplying energy for ADP transformation into ATP. Ultimately, during the dark reactions, produced ATP and NADPH facilitate the conversion of CO₂ into carbohydrates through the Calvin cycle.
Nature offers a remarkable blueprint for storing solar energy in fuels. Crucially, the essential mechanisms behind the Z-scheme concept, including light-induced charge separation, charge transfer, and reaction catalysis, have inspired the development and realization of artificial photosynthesis.22

![Figure 7](image_url)

**Figure 7. Simplified schematic illustration of the light reaction (Z-scheme) in natural photosynthesis. (Tyr = tyrosine; Pheo= pheophytin; Qa and Qb = Quinones A and B; Cyt b6f = an Fe-S Rieske center complex; PC = plastoquinone binding sites; A0 = chlorophyll II; A1 = phylloquinone; Fw/a/b = three separated Fe-S protein; FD = ferredoxin; FNR = ferredoxin-nicotinamide-adenine dinucleotide phosphate reductase; P680 and P700 = pigments with absorption maximum at 680 nm or 700 nm).**

As previously discussed, the conversion and storage of solar energy into chemical bonds, mimicking nature's remarkable photosynthesis process, presents an optimal solution to energy challenges. To achieve such solar-to-chemical energy conversion, three fundamental processes are imperative in a heterogeneous artificial photosynthesis system: (1) light absorption, (2) carrier transportation, and (3) the catalytic formation of chemical bonds (Figure 8a). In the light absorption phase, photons with energies surpassing the semiconductor's band gap induce the excitation of electrons, moving them from the occupied valence band (VB) to the unoccupied conduction band (CB), thereby forming separated charges (electrons and holes). Separated charge carriers in the bulk of the semiconductors are then transported to the surface/interface through drift and/or diffusion mechanisms. These charges can be utilized via two distinct methods: the direct and indirect approaches. In the indirect approach, the photo-induced separated charges are routed to the electrolyzer in the form of a direct current via wires (Figure 8b). In this scenario, the light-absorbing component is actually a PV cell, and the entire indirect photovoltaic-electrolyzer (PV-EC) configuration operates as a distributed system consisting of an independent PV cell and a separate electrolyzer. Conversely, the direct approach facilitates the immediate transfer of separated charges to the photoelectrode-electrolyte interface,
thereby triggering catalytic reactions (Figure 8c). The direct photoelectrochemical (PEC) cell configuration is a monolithic system with catalysts immobilized on photoelectrodes.

![Diagram of solar-driven water splitting](image)

**Figure 8.** (a) Main processes of solar-driven water splitting. (b) Schematic diagram of the photovoltaic-electrolyzer configuration. (c) Schematic diagram of the photoelectrochemical cell configuration.

Both direct and indirect approaches chemically store energy from sunlight in chemical bonds. Regardless of the chosen device configuration for solar fuel generation, the photogenerated carriers are ultimately transferred to the heterogeneous catalyst layers or electrodes to facilitate the respective catalytic reactions. Specifically in green hydrogen generation, the oxygen evolution reaction (OER) is driven by photogenerated holes at the anode, while electrons drive the hydrogen evolution reaction (HER) at the cathode. To sum up, the design of efficient light absorbers and active catalyst materials is pivotal in developing a high-performance heterogeneous artificial photosynthesis system. In this thesis, both the catalyst part and the light absorber part for (photo)electrochemical-driven water oxidation will be discussed.

### 1.2.2 Functional mimic: photovoltaic-electrolyzers

The PV and EC components can be treated as two independent parts in PV-EC devices where the light absorber is separated from the electrolyte. This separation allows for greater flexibility in terms of modularization and optimization (Figure 9a). A critical metric to assess the performance of solar
fuel devices is the solar-to-hydrogen (fuel) conversion efficiency (\(\eta_{\text{STH}}\)), defined by Equation 5.

\[
\eta_{\text{STH}} = \frac{J_{\text{op}} \, (\text{mA cm}^{-2}) \times 1.23 \, (\text{V}) \times \eta_F}{P_{\text{light}} \, (\text{mW cm}^{-2})}
\] (5)

Where \(J_{\text{op}}\) represents the operational current density at the intersection point, \(P_{\text{light}}\) is incident light power, and \(\eta_F\) signifies the faradaic efficiency. In the PV-EC configuration, the \(\eta_{\text{STH}}\) of the whole device can be treated as the product of the solar-to-electricity power conversion efficiency (PCE) of the PV module (\(\eta_{\text{PV}}\)) and the electrolyzer efficiency (\(\eta_{\text{EC}}\)). Correspondingly, efficient PV and electrolyzer devices are required to construct highly efficient PV-EC setups. As shown in Figure 9b, a higher \(J_{\text{op}}\) can be obtained by advancing a PV device with a higher short circuit current (\(J_{\text{sc}}\)), open circuit voltage (\(V_{\text{oc}}\)), and fill factor (FF). Despite considerable efforts in developing high-efficiency PV devices, single-junction PV cells often lack the photovoltage needed for overall electrocatalysis (exceeding 1.6 V). Hence, multijunction structures, analogous to the Z-scheme concept in natural photosynthesis systems, typically become essential for achieving bias-free PV-EC systems. Concurrently, minimizing overpotentials for both OER and HER, as well as reducing resistance losses in the electrolyzer, including contact, solution, and wire resistances, are equivalent pivotal strategies to enhance both \(J_{\text{op}}\) and \(\eta_{\text{STH}}\). A detailed discussion of PV devices is beyond the scope of this thesis and, as such, will not be elaborated upon herein; progress on water oxidation catalysts is elaborated upon in the subsequent text.

One significant advantage of PV-EC systems lies in their potential for realizing high \(\eta_{\text{STH}}\) values. Specifically, a double junction absorber system could achieve values up to 27%, given bottom and top absorber band gaps of 1.05 and 1.7 eV, respectively. Additionally, most technologies related to the PV and EC components are already well-developed and commercially available, making it feasible to construct large-scale plants using the current technology. Nevertheless, the inherent complexity of PV-EC systems tends to increase the \(H_2\) production costs compared to conventional fossil fuel-based methods. Therefore, the development of efficient yet cost-effective electrolyzer systems remains crucial in decreasing the levelized cost of hydrogen production. Furthermore, illuminated solar panels inherently experience heating, accounting for 75-96% of the absorbed solar energy. This heating often results in a decline in both output performance and lifetime. Consequently, devising an effective cooling strategy for photovoltaic panels is crucial for the prospective application in solar hydrogen production. An integrated configuration, as opposed to a separate
one, can be adopted for the PV-EC device, thereby mitigating the electrical and thermal losses typical of conventional distributed PV-EC systems by shortening wire and thermal management.\textsuperscript{31}

\textbf{Figure 9}. (a) Schematic diagrams of the PV-EC device. (b) The operation potential ($E_{op}$) that determined by the current-voltage (J-V) curve of the PV device and linear sweep voltammetry (LSV) curves of the electrolyzer.

1.2.3 \textit{Structural mimic: photoelectrochemical cell}

The PEC cell integrates functional materials into the electrodes, with the light-absorbing part directly attached to the catalytic part, eliminating the need for wire connections. This configuration utilizes two electrodes: the anode for OER and the cathode for HER. Instead of relying on an external electricity supply, the PEC draws power (driving force) directly from solar energy harvested by the photoelectrodes. Figure 10 illustrates the configurations of PEC cells. In its basic form, a photo-active electrode pairs with a counter electrode that solely functions as a catalyst. When an n-type semiconducting photoanode is connected to a counter electrode (e.g., platinum), electrons are extracted from water by light-induced charge-separation generated from the light absorbers. These electrons then move to the counter electrode, where the HER takes place (Figure 10a). Similarly, a p-type semiconducting photocathode can also serve as the photo-active center, as shown in Figure 10b.

The high thermodynamic requirements and sluggish proton and electron kinetics for O-O bond formation makes it challenging for single-junction semiconductor photoelectrodes used in most PEC cells to drive the water splitting reaction directly without the assistance of bias.\textsuperscript{32-35} Despite using high band gap semiconductor materials (over 2.0 eV), such as BiVO$_4$ and Fe$_2$O$_3$, coupled with relatively efficient catalysts, oxide semiconductor-based
PEC faces difficulty in providing sufficient driving force for the total water splitting reaction due to the mismatching of the energy band structure and limited photovoltages. The maximum theoretical $\eta_{STH}$ for a single absorber system is 11.2%, with a band gap of 2.26 eV (Figure 11a).\textsuperscript{24} The value falls far short of the 17% Shockley-Queisser limit,\textsuperscript{36} highlighting the substantial energy losses due to reaction overpotentials and charge recombination. Hence, discovering a single-junction semiconductor film that can produce sufficient photovoltage while efficiently capturing a significant portion of the solar spectrum, as well as optimizing device configuration and catalysts to minimize carrier recombination and catalysis overpotentials, remains an ongoing and complex challenge in PEC research. Chapter 5 of this thesis introduces a novel high band gap light-absorbing material, FAPbBr$_3$ (2.2 eV), suitable for photoanode construction. By optimizing the device structure and applying efficient catalysts, the as-fabricated monolithic FAPbBr$_3$ photoanode can provide record high photovoltages, significantly diminishing the reliance on auxiliary bias voltages.

![Schematic diagrams of PEC cells](image)

**Figure 10.** Schematic diagrams of PEC cells composed of a single light absorber and a counter electrode (CE): (a) photoanode + CE configuration and (b) photocathode + CE configuration. (c) Schematic diagram of the PEC tandem configuration. (d) The operation potential that determined by the J-V curves of the photoanode and photocathode. The Improved onset potential and increased saturation current can significantly increase STH efficiency.
To achieve unassisted PEC cells, a typical configuration inspired by the natural photosynthesis system, named photoanode-photocathode (or Z-scheme) tandem PEC cell, is presented in Figure 10c. In the described system, both the photoanode and photocathode are immersed in electrolytes and linked via an external circuit. Compared to single photoelectrode PEC devices, Z-scheme PEC cells incorporate two light-harvesting units: one facilitating the water oxidation reaction and another handling the hydrogen generation reaction. Z-scheme PEC enables the absorption of a broader spectrum and provides sufficient photovoltage for water splitting by combining the individual photovoltage of the two photoelectrodes in the system. The solar energy conversion mechanism of a Z-scheme PEC cell closely resembles that of natural photosynthesis. Both processes encompass common functional components, such as water serving as the electron/proton donor, dual light-harvesting centers with stepwise charge pumping processes, and analogous energy storage processes, with hydrogen mirroring NADPH and electricity analogous to ATP.

Theoretically, the PEC tandem cell offers superior $\eta_{\text{STH}}$ and negates the need for additional bias potentials. The intersection of the $J-V$ curves for both the photoanode and photocathode determines the $\eta_{\text{STH}}$ of the device (Figure 10d). The saturated current density for each photoelectrode constrains the maximal feasible catalytic current densities in the Z-scheme system. Correspondingly, reducing the band gap to expand the light utilization range can theoretically increase these currents. Moreover, the onset potential ($E_{\text{onset}}$) of these photoelectrodes is also a pivotal parameter dictating the operation current. A
higher band gap is conducive to the photoanode having a more negative onset potential, while the photocathode should exhibit a more positive onset potential. Consequently, selecting an optimal band gap to balance both the saturation current and onset potential is imperative. Theoretically, the tandem PEC configuration exhibits a maximum $\eta_{\text{STH}}$ exceeding 25% when paired with high-quality photoelectrodes with optimal band gap combinations ranging between 1.65-1.8 eV and 0.95-1.15 eV (Figure 11b). Developing materials that meet all necessary criteria, including appropriate band structures, intrinsic electronic properties, and stability, has proven to be a formidable challenge. As a result, the $\eta_{\text{STH}}$ values of current PEC devices still lag behind their theoretical potential.

PEC cells have garnered significant interest because of their reduced system complexity compared to PV-EC systems. To surpass the competitiveness of PV-EC systems, PEC devices are highly required to boast $\eta_{\text{STH}}$ greater than 10% and to have improved stability and scalability suitable for practical solar hydrogen production. Consequently, future fundamental research should prioritize the development of new Earth-abundant light-absorbing materials, the synthesis of cost-effective catalysts, the facile loading of catalysts, and the optimization of device architecture to facilitate charge transport. In this thesis, our efforts in designing novel light absorbers and elucidating the water oxidation mechanism will be demonstrated.

### 1.3 Water oxidation catalysis

The water oxidation reaction serves as an optimal anodic reaction, supplying electrons and protons for hydrogen production, CO$_2$ and N$_2$ reduction, and other electrochemical processes. As the main bottleneck of the water splitting reaction, the bond formation between two oxygen atoms during water oxidation necessitates the transfer of four protons and four electrons between two water molecules. Given the intricate nature of water oxidation, its kinetic process typically demands a significant overpotential ($\eta$).

$$\eta = E_{\text{applied}} - E^0$$  \hspace{1cm} (6)

Water oxidation reactions employing either homogeneous or heterogeneous water oxidation catalysts (WOCs) exhibit reduced overpotential and faster kinetics due to a reduced energy barrier. Homogeneous catalysts are synthetic metal complexes with structural and electronic properties modifiable through ligand and metal alterations. Conversely, heterogeneous catalysts encompass bulk materials, nanostructured materials—whether organic, inorganic, or hybrid—and molecular catalyst-immobilized electrodes, predominantly utilized as electrodes in electrolyzers.
1.3.1 Homogeneous water oxidation catalysts

Homogeneous catalysts (or molecular catalysts), especially ruthenium-based organometallic compounds, have attracted extensive attention due to their tunable structural and electrochemical properties, as well as the simplicity in investigating the proton-electron transfer mechanism during water oxidation by well-established methodologies. To trigger water oxidation, the catalyst must be oxidized to a potential higher than the thermodynamic requirements of water oxidation reactions ($E^0 = 1.23\text{ V vs. RHE}$ or $E^0 = 1.23 - 0.059 \times pH$ V vs. normal hydrogen electrode (NHE)). In homogeneous systems, such oxidation-driven force could be provided in a chemical or electrochemical manner. The most used chemical oxidants are ceric ammonium nitrate (CAN, Ce$^{IV}$) and sodium periodate (NaIO$_4$), while the electrochemical-driven force is provided by an inert electrode linked with a potentiostat.

The primary metrics for assessing the performance and stability of homogeneous catalysts are the turnover frequency (TOF) and turnover number (TON). These can be determined using the following equation:

$$\text{TON} = \frac{\text{Number of evolved O}_2 \text{ molecules}}{\text{Number of active sites}} \quad (7)$$

$$\text{TOF} = \frac{\text{TON}}{t} \quad (8)$$

Where $t$ is the reaction time. It is worth noting that a meaningful comparison of reported TOFs and TONs for molecular WOCs necessitates evaluation under consistent conditions, i.e., the same solution environment and the same driving force.

Noble metal-based molecular WOCs. When referring to the history of molecular WOCs, the “blue dimer”, the first well-known ruthenium WOC, was reported by the Meyer group in 1982 (1, Figure 12).$^{39}$ This catalyst features a binuclear ruthenium center linked by a $\mu$-oxo bridge. When driven by Ce$^{IV}$, it achieved a TON of 13 and a TOF of 0.004 s$^{-1}$. Despite the catalyst's limited stability and performance, it set an initial benchmark for molecular WOCs. Subsequently, binuclear Ru WOCs have advanced swiftly through tailored ligand design. Complex 2 exhibits a larger TON of 512 and TOF of 0.014 s$^{-1}$ toward Ce$^{IV}$-driven water oxidation by incorporating the rigid bpp- ligand ($H_{bpp} = 3,5$-di(2-pyridyl)pyrazole).$^{40}$ Thummel and co-workers reported a binuclear Ru WOC 3 based on a specific bis-tridentate ligand, and the performance of this catalyst was systematically improved with a TON of 538 and TOF of 0.046 s$^{-1}$. In 2005, Thummel and co-workers introduced the first mononuclear Ru WOC 5 with a TON of 260 and TOF of
0.014 s⁻¹. Its activity rivaled that of binuclear complexes, spurring interest in the design of mononuclear catalysts. This advancement enhanced the synthetic efficiency and offered a more concise system for studying catalytic mechanisms. Consequently, the development of mononuclear Ru WOCs gained substantial momentum.

![Figure 12](image)

**Figure 12. Structures of representative binuclear and mononuclear Ru-based WOCs.**

The OEC in PSII is bonding to amino residues that contain oxygen and nitrogen ligands, including carboxylate and imidazole groups. Especially, the surrounding electron-rich carboxylate could sufficiently stabilize high-valence states of the manganese cluster and are essential for effective water oxidation at a low overpotential. Inspired by this concept, catalysts with carboxylate ligands were formulated to augment the electron density at the metal center for reducing the onset potential. In 2009, the Sun group isolated an OER-active seven-coordinate ruthenium(IV) intermediate from a mononuclear complex 6 ([Ru(bda)L₂], bda²⁻ = 2,2’-bipyridine-6,6’-dicarboxylate; L = N-heterocyclic aromatic ligands). This famous molecule could trigger water oxidation with a high TON of 2000 and TOF of 41 s⁻¹.
Further modification of the axial ligands of the Ru-bda type catalysts enabled the highest TOF of 1000 s⁻¹ and the highest TON over 100000 (Figure 12). The approach of incorporating carboxylates can be extended to binuclear systems as well. For instance, catalyst 4 exhibits a superior overpotential, high activity (TOF = 1.2 s⁻¹), and prolonged durability (TON = 10400) in Ce⁴⁺-driven water oxidation compared to earlier binuclear Ru WOCs coordinated with only N-ligands. The Ru-bda configuration significantly enhances the performance of mononuclear catalysts, outperforming the OEC in PSII with a TOF ranging from 100 to 400 s⁻¹. Subsequent modifications with anionic ligands not only bolsters the stability and efficacy of these catalysts but also offers deeper insights into the structure-activity relationship of synthetic WOCs. Recently, substituting the carboxylate with sulfonate groups resulted in an exceptionally efficient electrochemical WOC that achieves a TOF of 12900 s⁻¹ under neutral conditions (calculated by plateau current analysis; see reference 53 for details).

Analogous to the Ru-N₄/O₂ moiety in Ru-bda type WOCs, the Ru-tda family with Ru-N₃/O₁ moiety is also a well-investigated electrocatalyst (tda²⁻ = 2,2’:6’,2’’-terpyridine-6,6’’-dicarboxylate). The inactive [Ru(tda)L₂] catalyst could be electrochemically activated to high-valent active Ru(O)-tda species under high potentials, which displays a TOFmax of 8000 s⁻¹ at pH 7 (calculated by the foot of the wave analysis, FOWA; see reference 55 for details). The uncoordinated dangling carboxylate group also acts as an intramolecular proton acceptor, facilitating the deprotonation of water molecules during the nucleophilic attack steps. Further modification of Ru-tda with phosphonic groups produced catalyst 9, which exhibited a TOFmax of 16,000 s⁻¹ under neutral conditions (as determined by FOWA). However, subsequent analysis revealed that this catalyst decomposed into RuO₂ and other inactive species, suggesting that the pyridyl carboxylate ligand is considerably much more stable than its phosphonate derivative. Very recently, the Sun group reported a Ru-tds WOC with sulfonate substitution (tds = 2,2’:6’,2’’-terpyridine-6,6’’-disulfonate). The dynamic coordination/de-coordination of the sulfonate group facilitates the formation of Ru-aqua active species, resulting in a high TOFmax of 12,000 s⁻¹ at pH 7 (as determined by FOWA).

**Non-noble metal-based molecular WOCs.** The advancement of molecular WOCs extends beyond just noble metals. Molecular WOCs based on 3d-transition metals, including Mn, Fe, Co, Ni, and Cu, have developed remarkably over the past few decades. The use of multidentate ligands is an important strategy to stabilize first-row transition metal complexes under...
catalytic conditions. In 2011, the Fillol and Costas groups reported various mononuclear iron complexes bearing the tetradentate alkylamine-pyridine type ligands. Among these, complex 12 exhibits superior activity, achieving a TOF of 0.23 s\(^{-1}\) and a TON of 360 in Ce\(^{IV}\)-driven water oxidation (Figure 13). The authors emphasized the critical role of two free cis-coordination sites for optimal water oxidation reactivity and highlighted that the reduced coordination rigidity and diminished ligand basicity of backbone ligand are paramount to enhancing the catalytic activity within this category of complexes. In 2012, the Berlinguette group reported the first example of cobalt WOC 13 using modified PY5 as a ligand (PY5 = 2,6-(bis(bis-2-pyridyl)-methane)-pyridine). With a Co-N\(_5\)/O\(_1\) moiety, this complex demonstrates a catalytic onset overpotential of 500 mV at pH 9.2. In 2014, the first nickel WOC, 14 in Figure 13, was reported by Lu and co-workers. This complex shows a maximum electrolytic current of 0.9 mA cm\(^{-2}\) at an overpotential of 750 mV in a neutral NaPi buffer. The O-O bond formation proceeds through an intramolecular coupling pathway. In 2012, Mayer and co-workers reported the first example of a mononuclear copper WOC, Cu(bpy)(OH)\(_2\) 15, bpy =2,2′-bipyridine). The results demonstrate that the straightforward bpy-coordinated molecule functioned effectively as a robust homogeneous WOC, achieving a TOF of 100 s\(^{-1}\) when driven by electrochemistry.

Figure 13. Structures of representative mononuclear and multinuclear 3d-transition metal-based WOCs.
The natural OEC that catalyzes the water oxidation reaction contains a multinuclear Mn$_4$CaO$_5$ complex as the active center. Therefore, synthetic multinuclear 3$d$-transition metal complexes are anticipated to be excellent candidates for developing efficient WOCs. The landmark multinuclear iron WOC 16, which consists of the [Fe$_3$(μ$_3$-O)] core wrapped by two [Fe(μ-bpp)$_3$] units, was presented by the Masaoka group. The two apical Fe atoms, which are six-coordinate, are anticipated to function as adjacent water activation sites. Conversely, the other three Fe atoms in between, which are five-coordinate, are likely the active sites for water binding and O-O bond formation. Remarkably, under neutral conditions, this pentanuclear catalyst exhibits a high TOF of 1400 s$^{-1}$ (as determined by plateau current analysis), placing it at the best among iron-based electrocatalysts. It is imperative to note that subsequent research on this pentanuclear cluster, conducted by both the Allakhverdiev and Najafpour groups as well as the Llobet group, suggests that the in-situ formation of iron oxide might account for the rapid kinetics. Inspired by the cubane-like structure of the OEC, Dismukes and co-workers reported the first example of a cobalt cubane (complex 17) demonstrating catalytic activity for water oxidation in 2011. Under photoirradiation, employing [Ru(bpy)$_3$]$^{2+}$ as a photosensitizer and Na$_2$S$_2$O$_8$ as an electron acceptor, the TOF and TON values for the reaction were calculated to be 0.02 s$^{-1}$ and 40, respectively. Subsequent mechanistic investigations, drawing upon both experimental results and density functional theory (DFT) calculations, indicated that the O-O bond forms through the nucleophilic attack of the hydroxy anion on the Co(V) =O intermediate. Applying a multinuclear strategy to copper, the Liao and Zhang groups reported a trinuclear copper cluster 18 that exhibits an exceptional TOF of 20000 s$^{-1}$ (determined by plateau current analysis) and 61374 s$^{-1}$ (determined by FOWA) in sodium bicarbonate solutions, placing it at best among other non-precious metal-based WOCs. The study underscores multinuclear design as an effective strategy to regulate O-O bond formation in water oxidation catalysis.

1.3.2 Water oxidation mechanisms over homogeneous systems

Water oxidation catalysis, recognized as the rate-limiting bottleneck in artificial photosynthesis, is central to solar fuels, offering the essential source of electrons and protons for converting solar energy into chemical energy. Investigating molecular WOCs, serving as model complexes, provide not only insights into structure-performance correlations vital for designing industrially valuable heterogeneous WOCs, but also augments the comprehension of O-O bond formation mechanisms.
The catalytic cycle of water oxidation comprises four primary steps: water binding, water activation, O-O bond formation, and oxygen release (Figure 14). The water binding step is not required for the catalysts that already incorporate pre-coordinated aqua ligand(s). However, for those catalysts with all six coordination sites occupied by ancillary ligands and devoid of water molecules in the coordination sphere, the initial water binding spontaneously occurs when the metal center achieves a high chemical valence (e.g., Ru\(^{2+}\) to Ru\(^{3+}\) in WOC 6).

**Figure 14.** Overview of WNA and I2M mechanisms for water oxidation.

**Activation of water.** The initial stage of any WOC mechanism necessitates the oxidative activation of the binding water molecule, leading to the formation of either metal-oxo or metal-oxyl species. This process typically involves multiple proton-coupled electron transfer (PCET) steps with several protons and electrons being removed. As illustrated in Figure 15a, the PCET processes can occur either in a concerted or sequential fashion, depending on the redox potential (E\(^0\)) and acid dissociation constant (K\(_a\)) of each reaction intermediate. The PCET process can be intuitively illustrated in the potential-pH (Pourbaix) diagram for the specific redox pair. For a redox with concerted proton-coupled electron transfer (CPET) feature, the discrepancy in pK\(_a\) values between oxidized and reduced species (ΔpK\(_a\)) results in the oxidation potential shifts upon protonation/deprotonation (ΔE\(^0\) = 0.059 × ΔpK\(_a\) at 298K) (Figure 15b). This shift aligns with the Nernstian slope for the apparent potential of a pH-dependent 1H\(^+\)/1e\(^-\) process in the Pourbaix diagram. Such coupled deprotonation may avoid charge build-up that would make each successive redox step increasingly difficult in multi-redox reactions and allow for several oxidation steps in a narrow potential range.\(^{71}\) Redox potentials for electron transfer (ET) controlled processes do not show pH dependency in the Pourbaix diagram.
The factors that influence the redox potential and $pK_a$ of water activation intermediates play a pivotal role in determining the catalytic properties of a catalyst. The primary coordination sphere, where the coordination sites in ligands are directly bonded to the metal, is responsible for the structural and electronic tuning of the metal sites. Engineering the ligand structure is a potent strategy to adjust both the redox characteristics and the catalytic behavior. For instance, as discussed in section 1.3.1, enhancing the electron density of Ru center through the incorporation of negatively charged carboxylates serves as a prime example. Complexes $^{19,72}20,^{73}$ and $^{645}$ exhibit similar coordination geometries but feature varying carboxylate substituents (Figure 16a). Modifying the quantities of the carboxylate ligands significantly affects the electron-donating attributes of the backbone ligands, subsequently leading to reduced potentials of the redox processes in water activation (Ru$^{2+/3+}$, Ru$^{3+/4+}$ and Ru$^{4+/5+}$ couples) (Figure 16b). These alterations further impact the rate of oxygen evolution, as demonstrated by the escalating TOFs (Ce$^{IV}$-driven) associated with enhanced electron-donating capacity (Figure 16c).
Figure 16. (a) Structures of Ru-bda-type WOCs with variable amounts of carboxylate groups. (b) The corresponding redox potentials at pH 1 vs. NHE and (c) CeIV-driven TOFs. (d) Structures of Ru-bda-type WOCs with different negatively charged ligands. (e) The corresponding redox potentials at pH 1 vs. NHE. (f) Structures of Ru-bda-type WOCs with N-substituted bda ligands. (g) The corresponding redox potentials at pH 1 vs. NHE and (h) CeIV-driven TOFs. Adapted with permission from reference 74. Copyright 2022, American Chemical Society.
The electron-donating ability could further be modulated by altering the groups on the bipyridine ligand. Among complexes 6, 10, 21, the one with the strongest electron-donating group exhibits the lowest redox potentials for activation of water (Figure 16e). In contrast, the weaker electron-donating sulfonate substituent leads to the highest potential. As a result, complex 6 achieves the highest TOF in CeIV-driven water oxidation. However, the sulfonate-substituted complex 10 demonstrates superior electrochemical water oxidation performance compared to complex 6. This indicates that the oxidation method and the solution environment profoundly influence the catalytic mechanism and water oxidation performance. The electronegativity can be also tuned by introducing additional electron-withdrawing/donating substituents such as bromo, carboxylic acid, and trifluoromethyl. An elegant example of the influence of electronics on equatorial ligands involves substituting the pyridine unit with its structural analog, pyrazine (Figure 16f). This substitution also prevents steric conformational variations by avoiding the addition of groups to the back side of the bda ligand. Nitrogen substitution led to a reduction in its electron density. As a result, sp2-N-substituted Ru-bda complexes 22 and 23 exhibit higher redox potentials for the Ru2+/3+ wave compared to the original complex 6 (Figure 16g). While the higher oxidation states (Ru4+/5+) remain largely unaffected under acidic conditions, similar TOF values for complexes 6, 22, and 23 suggest that electronic modifications to the bda equatorial ligands did not significantly impact their catalytic properties (Figure 16h). The result rationalized that the Ru2+/3+ redox potential minimally impacts the catalytic performance, as water binding for Ru-bda-type WOCs usually takes place at the Ru3+ state. DFT calculations further revealed that incorporating nitrogen atom(s) into the bda backbone only results in minimal differences in geometry, spin density, and charges of the high-valent reactive Ru5+=O. Consequently, electronic effects exert a negligible impact on the reactivity of the high-valent Ru oxyl intermediate.

To optimize catalysts, controlling the two interconnected factors, E0 and Ks, is essential. This control extends beyond electronic modulation to include aspects like coordination distortion and hydrophilic/hydrophobic balance. The regulation of the PCET behavior of high-valent metal-oxo species is of particular significance. Based on the preceding discussion, one can deduce that the electronic and structural impacts of backbone ligands in different WOCs must be assessed step-by-step on a case-by-case basis.

**O-O bond formation.** The O-O bond formation step theoretically accounts for 71% of the energy consumption in the entire oxygen evolution cycle, making it the most energetically demanding component of the overall
Consequently, the O-O bond formation is typically identified as the rate-determining step (RDS) of OER.

**Figure 17.** Representative O-O bond formation steps and corresponding catalysts for water oxidation.
Generally, there are two widely accepted O-O bond formation pathways for molecular WOCs as described in Figure 14: the formation of M=O species can proceed either the interaction of two metal-oxos (I2M) or a water nucleophilic attack (WNA) for the crucial O-O bond formation step. In more detail, the mechanisms can be classified into three primary categories: single-site, bimolecular dual-sites, and unimolecular dual-sites (Figure 17).\cite{70, 80} The single-site category encompasses mechanisms such as the typical WNA with solution-mediated atom-proton transfer (APT)\cite{41, 56, 61, 81} and intramolecular hydroxyl coupling (IHC).\cite{63} The bimolecular dual-sites category includes the typical intermolecular I2M\cite{45-47, 54} mechanism and the bimolecular hydroxyl coupling (BHC)\cite{82} pathway. In contrast, the unimolecular dual-sites category, which is exclusive to specially designed double or multi-center WOCs, comprises mechanisms like intermolecular oxo/oxyl coupling (IOC)\cite{83}, redox isomerization (RI)\cite{84, 85}, intramolecular interaction of two metal-oxos (i-I2M)\cite{40}, and WNA with intramolecular atom-proton transfer (i-APT). Based on the distinct relay sites, i-APT mechanisms can be further categorized into those mediated by a base site,\cite{41, 56} metal-oxo/oxyl site,\cite{39} and preorganized water.\cite{86, 87}

APT. In the WNA pathway, following water activation, oxygen generation still necessitates multi-step proton transfer (PT) processes, accompanied by oxidation processes that can occur either stepwise or as concerted proton-coupled electron transfer. Figure 18 illustrates potential modifications to the O-O bond formation mechanism when introducing sequential proton-electron transfer steps. Various reaction pathways, including both decoupled and concerted elementary steps, can thus be conceivable.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{PCET_steps}
\caption{Schematic PCET steps during the O-O bond formation processes.}
\end{figure}
The pH dependence of the water oxidation activity varies based on whether the PCET process in O-O bond formation is concerted or sequential. Such pH dependence can thus serve as a crucial tool for identifying the details of PCET in the RDS of water oxidation. Different from the Pourbaix diagram of redox couples that only involves pH and thermodynamic parameter $E^0$, this pH dependence activity should also consider the kinetic issue caused by that the driving force varies with pH. A detailed derivation and explanation will be provided in Chapter 2.

![Figure 19. Acid dissociation constant of water and typical buffer ions.](image)

Upon the WNA mechanism, the pivotal step involves the nucleophilic attack of a water molecule on an electron-deficient metal-oxo, with simultaneous proton transfer to an external/internal proton acceptor, resulting in a hydroperoxide intermediate. Within this process, the simultaneous oxygen-atom transfer and proton transfer, termed atom-proton transfer, highlights the importance of the accompanying concerted proton transfer in avoiding a high-energy protonated peroxodic intermediate. The property of the proton acceptor significantly affects the catalytic behavior in APT-controlled O-O bond formation. When the APT is mediated by the reaction solution (i.e., external proton acceptor), significant rate enhancements can be observed with added proton acceptor bases (B).

$$k_{\text{obs}} = k_o + k_B[B] \quad (9)$$

The first order in base concentration [B], along with the dependence of $k_B$ on base strength, aligns with the APT equilibrium in Equation 11. The acid dissociation constant of buffer ions indicates base strength (Figure 19), which is closely related to the value of $k_B$ in solution-mediated APT. Under acidic conditions, water directly acts as a poor proton acceptor in the reaction (Equation 10), even if $pK_a(H_2O^+) = -1.7$, indicating a small $k_B$ and sluggish kinetics. In a buffered solution, $k_B$ demonstrates a dependency on the $pK_a$ value of buffer ions, as evidenced by $k_B$ values of 3.8, 10.3, and 48 M$^{-1}$ s$^{-1}$ for $H_2PO_4^-$ ($pK_a = 2.2$), acetate ($pK_a = 4.8$), and $HPO_4^{2-}$ ($pK_a = 7.2$), respectively, with $[\text{Ru}^V(\text{tpy})(\text{Mebim-py})(\text{O})]^3+$ WOC. At higher pH, despite the kinetically significant concentration of $OH^-$, it should not be treated as an independent molecule in the solution reaction since $OH^-$ in solution exists...
within a hydrogen-bonded network, solvated by water molecules, and potentially coordinating with cations. In the context of alkaline OER, $\text{H}_2\text{O}$ and $\text{OH}^-$ are functionally equivalent reactants due to the "shared" proton, as illustrated in Equation 12. Given that the transferred proton can be conceptualized as being equally distributed between two molecules, $\text{OH}^-$ emerges as an excellent base with a high $pK_a$ of 15.7 (Equation 13), analogous to the scenario presented in Equation 11 for buffered conditions.

\[
\begin{align*}
\text{Acid:} & \quad \text{M}=\text{O} + \text{H}_2\text{O} + \text{H}_2\text{O} & \quad \text{M}=-\text{O} - \text{O} \quad \text{H} \quad \text{H} & \quad \text{M}=-\text{O} - \text{O} \quad \text{H} \quad \text{H} & \quad \text{M}=\text{OOH} + \text{H}_3\text{O}^+ & (10) \\
\text{Buffered:} & \quad \text{M}=\text{O} + \text{H}_2\text{O} + \text{B}^- & \quad \text{M}=-\text{O} - \text{O} \quad \text{H} \quad \text{H} & \quad \text{M}=-\text{O} - \text{O} \quad \text{H} \quad \text{H} & \quad \text{M}=\text{OOH} + \text{HB} & (11) \\
\text{Basic:} & \quad \text{M}=\text{O} + \text{H}_2\text{O} + \text{OH}^- & \quad \text{M}=-\text{O} - \text{O} \quad \text{H} \quad \text{H} & \quad \text{M}=-\text{O} - \text{O} \quad \text{H} \quad \text{H} & \quad \text{M}=\text{OOH} + \text{H}_2\text{O} & (13)
\end{align*}
\]

*i-APT*. Rate enhancements with external buffers that arise from APT pathways can augment reactivity and facilitate water oxidation kinetics. Likewise, intramolecular proton transfer sites, often referred to as "proton relays", including dangling base sites and neighboring metal-oxo/oxyl sites, can also accelerate the proton transfer process and stabilize charged intermediates through the $i$-APT mechanism. The role of dangling base sites in enhancing water oxidation reactions has been explored in various reports, with studies focusing on sites including phosphate, carboxylate, sulfonate, and pyridine. These internal proton relays within the secondary coordination sphere might outperform external ones in the outer spheres, provided that they operate within appropriate pH ranges. The neighboring metal-oxo site ($\text{Ru}^{5+}=\text{O}$) in the blue dimer 1 has been demonstrated to...
effectively shuttle a proton from the water molecule during its nucleophilic attack on the parallel metal-oxo site.\textsuperscript{101, 102} This metal-oxo-mediated $i$-APT process may elucidate the synergistic effect observed in binary or multi-metal material WOCs, where specific metal-oxo/oxyl/hydroxyl sites potentially act as proton relays during the reaction.

\textbf{Figure 20.} (a) Structures of Ru-bda-type WOCs with water network-mediated proton transfer. (b) Proposed H-bonded network around the catalytic site for WOC 29. Adapted with permission from reference 87. Copyright 2022, Wiley-VCH. (c) Proposed key intermediates at the Ru$^{5+}$ state of the water oxidation cycle for WOC 30 at pH 1. Adapted with permission from reference 86. Copyright 2022, Springer Nature.

Another approach to regulating the proton transfer is creating a controlled microenvironment near the catalytic site, which allows the preorganization of a water network to facilitate proton shuttling. The single-crystal structure of WOC 28 in its Ru$^{3+}$ state revealed a "ready-to-go" aqua ligand captured by the tri-ethylene glycol-based distal ligand, with a Ru-O distance of 3.62 Å (\textbf{Figure 20a}).\textsuperscript{103} This offers insight into how substrate preorganization occurs within a water network that is arranged by a tailor-designed microenvironment in the outer coordination sphere. The follow-up study with WOC 29 showed that introducing hydrophobic outer-sphere interactions could stabilize high-valent intermediates and promote proton transfer in the WNA pathway, affirming the water network-mediated proton transfer
strategy for the APT process (Figure 20b). Following this concept, WOC 30 with a bipyridine-functionalized distal ligand was observed to more efficiently preorganize the hydrogen-bonding network (Figure 20c). Such a design, featuring a catalytic pocket that preorganizes substrate water molecules via a ligand positioned opposite the metal center, could boost WNA-controlled oxygen evolution to TOF of 140 s⁻¹ under Ce⁴⁺-driven conditions.

I2M. In the I2M pathway, radical coupling between two metal-oxo radical species (Mⁿ=O ↔ Mⁿ⁻¹-O•) leads to the generation of peroxide-bridge M-O-O-M species. The I2M mechanism is favored by electron-rich catalysts that possess greater oxyl radical character in their activated states. Then catalysts operating via this pathway can function at lower potentials, given that they do not necessitate a highly electrophilic M=O species and additional proton transfer steps following water activation. The coupling of two M=O moieties in the I2M mechanism can occur either intermolecularly (bimolecular) between separate molecules or intramolecularly (i-I2M) within multinuclear complexes. The intermolecular coupling necessitates that the radicals converge in a head-to-head manner, featuring short bimetallic distances and strong spatial interactions. Such bimolecular steps are particularly sensitive to catalyst concentration; catalysts that rely on intermolecular I2M will experience rate limitation at low concentrations. The best example of bimolecular O-O coupling with Ru-based catalysts is the Ru-bda systems reported by the Sun group. The kinetics of the Ru-bda family are dominated by secondary interactions via axial ligands. The increasing favorable secondary interactions of ligands, including hydrophobic, π-π, CH-π, and electrostatic interactions were found to change the bimetallic configuration, which consequently promote the intermolecular I2M approach (Figure 21). These interactions can also serve to immobilize molecular WOCs onto carbon-based substrates, such as carbon nanotubes or graphene, thereby facilitating the heterogenization of these catalysts.

The proposed i-I2M mechanism serves as the guiding principle behind the design of the binuclear WOCs, like the blue dimer (1), where two proximal metal-oxo groups are anticipated to engage in O-O coupling and subsequent oxygen evolution. However, most of the binuclear catalysts, including the mentioned blue dimer, follow the single-site pathway, suggesting that the optimal spatial arrangement of the bimetallic center plays a pivotal role in the coupling process. A clear illustration of intramolecular O-O coupling was provided by Llobet and co-workers with WOC 2. In this design, the equatorial ligand positions the activated Ru⁵⁺=O groups facing each other in an almost ideal position for O-O coupling.
Figure 21. Proposed π-π (left) and electrostatic (right) interactions between Ru-bda catalysts during the O-O bond formation process via the I2M pathway.

**Perspective.** Investigating the water oxidation mechanisms of homogeneous WOCs is instrumental in advancing heterogeneous WOCs for industrial water splitting applications. Despite extensive studies, the precise mechanisms underlying O-O bond formation in homogeneous systems remain incompletely understood. While a systemic understanding of O-O bond formation in ruthenium-based molecular WOCs has been established, applying this knowledge to non-noble metal complexes or even material systems remains challenging due to the disparate core-orbital structures of the metals. This gap, exacerbated by a lack of direct experimental evidence, rendered mechanistic investigations more difficult but meaningful. The final stage of the water oxidation cycle is the release of dioxygen and the re-entry of the catalyst into the catalytic cycle. In terms of free energy, the oxygen release step is substantially less demanding than the O-O bond formation step. Its faster kinetics complicate the experimental investigations, as only a limited number of intermediates have been isolated to date.\textsuperscript{112, 113} Consequently, this necessitates a greater reliance on computational analyses, highlighting considerable opportunities for future advancements. Although this focus has largely been on purely homogeneous systems, making molecular WOCs better than ever through identifying core design principles and challenges still holds practical relevance for related ubiquitous PCET reactions.

**First-coordination sphere engineering.** The first coordination sphere governs the structural and electronic modulation of the metal sites (Figure 22a). The employment of negatively charged ligands, coordination-distorted ligands, or adaptive ligands has been established as effective design principles for
ruthenium-based WOCs. These ligand engineering allow for the fine-tuning of water activation properties and O-O bond formation mechanisms through strategic equatorial and axial ligand design. Additionally, the synergistic interaction among multiple metals has been demonstrated to facilitate multi-electron and proton transfers, which are essential for accelerated water oxidation. Meanwhile, introducing redox-active ligands and multinuclear structures to accumulate positive charges during oxidation enables the stabilization of high-valent metal sites generated in the catalytic process and reduces the overpotential requirements.

**Figure 22.** Schematic diagrams of modifications on (a) the first coordination sphere and (b) the second coordination sphere of molecular WOCs. (c) Schematic diagram of heterogenization of molecular WOCs by polymeric strategy.

**Secondary-coordination sphere engineering.** The secondary coordination sphere plays a role in accelerating atom transfer, modulating catalyst-reactant or catalyst-catalyst interactions, and tuning the local microenvironment essential for water oxidation (Figure 22b). The dangling carboxylate, phosphate, sulfonate, pyridine, and pyridine oxide groups serve as proton and oxide relays, facilitating the transfer of protons/oxides and stabilizing the positively charged intermediates during the catalytic process. The
enhancement of secondary interactions of axial ligands, such as hydrophobic, π-π, CH-π, and electrostatic interactions, has been observed to alter the bimetallic configuration, thereby facilitating the intermolecular I2M approach in Ru-bda-type WOCs; while modifying backbone ligands could potentially shift the reaction from the I2M pathway to the WNA pathway, highlighting the significant interplay between intermolecular interactions in the solution and the underlying catalytic mechanism. Furthermore, the local water microenvironment near the catalytic center(s) is increasingly acknowledged to be crucial in modulating reaction rates and pathways. Water oxidation kinetics can be accelerated by employing pocket-shaped ligands with variable hydrophilic/hydrophobic or pyridinic sites featuring the capability of water network preorganization. While it is challenging to delineate the distinct functions of each component within a specific coordination sphere due to their interdependent effects, it is clear that research into the secondary coordination sphere is far from exhaustive, presenting ample opportunities for further investigations.

**Heterogenization engineering.** A multitude of techniques have emerged for immobilizing molecular catalysts on the functional electrodes, including those made of carbon and conductive metal oxides, via both covalent and non-covalent attachments. These approaches aim to construct efficient and stable devices for photoelectrochemical-driven electrolysis. However, its application remains limited by the instability of the anchoring groups and unfavored charge transfer barriers. In contrast, integrating molecular catalysts into heterogeneous polymeric materials that feature a combination of high stability, chemical versatility, and flexibility in installation of metal sites offers a viable solution to the heterogenization issue. Progress has been made in developing diverse support materials capable of anchoring isolated molecular single-metal sites. However, most of these support materials exhibit non-uniform characteristics, such as size and edge variations, resulting in distinct chemical environments surrounding the metal centers. This inherent heterogeneity hampers their utility in investigations of catalytic mechanisms and potential applications. Consequently, a well-defined catalytic system that can provide definite coordination environments to form structurally defined transition-metal active sites is essential for conducting reliable mechanistic studies in heterogeneous WOCs. Specifically, conductive, periodic, chemically stable polymers, such as metal-organic frameworks (MOFs) and covalent organic frameworks (COFs), can offer numerous uniform coordination sites, which are indispensable for the fabrication of molecular transition metal sites-grafted heterogeneous catalysts with uniform chemical environments and virtually non-existent structural evolution (**Figure 22c**). In this context, a molecularly well-defined
heterogeneous cobalt-based WOC was reported in Chapter 4, and the kinetic features of the molecular sites were systematically investigated. With such a conceptual framework now clearly established, various polymeric materials can be explored as versatile platforms for mechanism investigations, potentially leading to improved performance. Pushing the knowledge and insights from homogeneous systems to well-defined heterogeneous WOCs could unlock unprecedented opportunities. In summary, a wealth of research possibilities would intersect at the nexus of molecular and polymeric WOCs.

1.3.3 Heterogeneous water oxidation catalysts

Although molecular WOCs have shown exceptional water oxidation activity, their poor stability under reaction conditions hampers their practical application in water splitting systems. To date, heterogeneous WOCs based on transition metals have garnered significant attention due to their exceptional catalytic performance and robust stability in OER. Advanced heterogeneous WOCs can generally be categorized into two groups based on the scale of the active species: bulk inorganic materials and atomically dispersed materials. Additionally, immobilized molecular catalysts can be considered a subset of heterogeneous catalysts, even though their intrinsic active sites are derived from homogeneous molecular catalysts (Figure 23).

Figure 23. Schematic diagrams of heterogeneous WOCs.
Oxides. Despite their high cost, noble-metal-based material catalysts are considered the most effective for OER. Given the high activities at a wide pH range during water oxidation catalysis, noble-metal oxides like IrO\textsubscript{2} and RuO\textsubscript{2} are commonly selected as the benchmark electrocatalysts. However, RuO\textsubscript{2} exhibits significant instability in both acidic and alkaline electrolytes at elevated anodic potentials. While IrO\textsubscript{2} can endure higher anodic potentials and offers improved stability compared to RuO\textsubscript{2}, it is still not entirely free from stability concerns.\textsuperscript{119} Even though catalysts based on ruthenium and iridium are commonly used in water electrolyzers, their limited reserves pose a significant barrier to large-scale applications. The growing technological demands for low-cost heterogeneous WOCs have motivated intense research aimed at developing catalysts made exclusively from Earth-abundant elements.

Transition metal oxides have attracted widespread research interest in the fields of energy storage and conversion due to their low cost, abundant availability, and corrosion resistance. The multiple oxidation states commonly found in these oxides, specifically from M\textsuperscript{2+} to M\textsuperscript{4+} states, are considered to be active for water oxidation catalysis, making them highly promising for the development of efficient WOCs.\textsuperscript{120, 121} The water oxidation activity of transition metal oxide materials is highly dependent on various properties, including morphology, composition, oxidation states, number of 3\textit{d} orbital electrons, and surface oxygen binding energy, etc.\textsuperscript{122} The perovskite (ABO\textsubscript{3}) and spinel (AB\textsubscript{2}O\textsubscript{4}) type metal oxides have been demonstrated to exhibit high electrical conductivity, stable structures, and significant catalytic activity for water oxidation. Moreover, their adaptable structures feature transition metals in diverse coordination settings and varying oxidation states, enabling tunable OER performance by, for example, composition engineering, crystal facet control, morphology engineering, defect engineering.\textsuperscript{123, 124}

To meet the operational requirements of commercial electrolyzers, which mandate high conductivity, these water splitting devices typically function in either concentrated acidic or alkaline environments.\textsuperscript{125, 126} Mn, Fe, Co, and Ni-based oxides are known to demonstrate superior stability and activity towards OER when operating in alkaline conditions which makes them particularly suitable candidates for sustainable and efficient alkaline water electrolysis.\textsuperscript{127} Cobalt oxides (CoO\textsubscript{x}), possessing multiple oxidation states of Co\textsuperscript{2+/3+/4+}, have garnered significant attention for their application in catalyzing OER.\textsuperscript{120, 121, 128} It is widely believed that the phase transition from oxide to hydroxide in cobalt-based materials during the water oxidation process is key to their catalytic activity.\textsuperscript{129} Notably, the inorganic WOC of
Co-Pi, prepared from cobalt phosphate solutions, exhibits outstanding catalytic performance in neutral pH conditions. Subsequent characterizations confirmed that the active component of Co-Pi is cobalt oxide. Similarly, nickel oxide (NiO) has also received extensive attention in the field of electrocatalytic water oxidation. The catalytic activity of NiO has been incrementally enhanced through the adjustment of particle size, specific surface area, and surface microstructure. The introduction of other metals, such as iron and cobalt, into NiO can further elevate the water oxidation catalytic activity of NiO-based materials. Manganese is another element abundant in nature, featuring a diverse range of oxidation states from Mn$^{2+}$ to Mn$^{7+}$. Its oxide, MnO$_x$, also exhibits excellent catalytic activity for water oxidation in alkaline electrolytes. The catalytic performance of MnO$_x$ is largely dependent on various factors such as its crystal structure, morphology, porous architecture, and chemical composition. The water oxidation activity sequence of MnO$_2$ is $\alpha$-MnO$_2$ > amorphous MnO$_2$ > $\beta$-MnO$_2$ > $\delta$-MnO$_2$. The higher water oxidation catalytic activity of $\alpha$-MnO$_2$ can be attributed to multiple factors, including the presence of mixed valence states, an abundance of di-$\mu$-oxo bridges, and lower charge-transfer resistance. While many Earth-abundant OER-active materials like oxides of Mn, Fe, Co, Ni, and Cu oxides typically cannot survive at acidic conditions, there are exceptions, such as $\gamma$-MnO$_2$, Fe$_2$O$_3$, Co$_3$O$_4$, Co$_2$TiO$_4$, and CoFePbO$_x$, have demonstrated both stability and activity in such conditions, which is crucial for enhancing both the cost-effectiveness and compatibility of acidic proton-exchange membrane (PEM) electrolysers.

**Hydroxides.** Apart from conventional metal oxides, Fe, Co, and Ni-based transition metal hydroxides are another category of catalytically active materials for water oxidation reactions in alkaline conditions. Notably, surface reconstruction triggered by electrochemical processes to generate hydroxides has been commonly identified in various metal oxides when exposed to anodic potentials. This hints that the true active sites in oxide-based WOCs might be related (oxy)hydroxides species. Typically, the hydroxides are characterized by lamellar crystalline structure, with the metal layers and anion layers alternately stacked, which affords them a high specific surface area. This structural advantage results in more exposed active sites that are accessible for the reaction and offer the flexibility of fine-tuning their compositional elements and electronic properties. Such modifiability provides additional possibilities to optimize the catalytic performance, making these Fe, Co, and Ni-based hydroxides a versatile and promising class of catalysts for water oxidation applications.
Prior to the in-depth exploration of layered double hydroxides (LDHs) for water oxidation, single metal hydroxides, especially Ni(OH)$_2$, were considered as catalytically active materials.\textsuperscript{140} Yet, as research progressed, it became evident that iron impurities from the KOH electrolyte could be incorporated into the Ni(OH)$_2$ film during the electrochemical aging process, while this incorporation played a pivotal role in enhancing the water oxidation performance of Ni(OH)$_2$.\textsuperscript{141, 142} Inspired by this finding, researchers developed a range of high-performance WOCs based on Ni-Fe LDH materials.\textsuperscript{143-145} Although the incorporation of Fe enhances the catalytic performance, the reaction mechanism and the assignment of catalytic active sites remain contentious. Recent findings suggest that Ni undergoes oxidation to the +4 state, and the active oxygen species responsible for OER are believed to be associated with Ni sites.\textsuperscript{146-149} Conversely, high valent Fe$^{4+}$ has also been identified as active in OER, proposing catalytic cycles based on redox-active Fe sites.\textsuperscript{150-154} The exact synergistic interaction between Ni and Fe and the determination of catalytic active sites in Ni-Fe systems, however, remains unclear to date.

Beyond Ni-Fe LDHs, a range of metals have been incorporated into nickel hydroxides to optimize the catalytic performance for water oxidation.\textsuperscript{155-157} Moreover, cobalt-based layered hydroxides have also been extensively studied, with researchers attempting to introduce first-row transition metals like V, Mn, Fe, Ni, and Zn into cobalt-based layered hydroxides to enhance catalytic properties.\textsuperscript{158-160} As the understanding of layered hydroxides increases, there is a growing interest in using ternary,\textsuperscript{161-163} quaternary,\textsuperscript{164} and even high-entropy\textsuperscript{165} formulations of layered hydroxides as heterogeneous WOCs. Furthermore, the activity of hydroxides is significantly shaped by factors, such as the pH,\textsuperscript{166} the alkali cations present in the electrolyte,\textsuperscript{167} and the interlayer anions.\textsuperscript{168} This complexity gives LDH systems a challenging yet vast potential for research exploration.

**Chalcogenides, pnictides, and alloys.** A range of non-oxide materials, including transition metal chalcogenides, nitrides, phosphides, and even transition metals and their alloys, have been widely employed as WOCs.\textsuperscript{127, 169, 170} Transition metal chalcogenides, pnictides, and alloys generally exhibit more favorable electrochemical properties than their oxide counterparts, primarily because of their enhanced charge transfer kinetics and 3D porous structure.\textsuperscript{171-173} However, during water oxidation catalysis, the surfaces of these non-oxide materials often undergo \textit{in-situ} transformations into metal oxides or hydroxides.\textsuperscript{138, 174} Notably, these transformed metal oxides or hydroxides are the actual active species driving catalytic activity, while the original non-oxide materials serve as conducive substrates, promoting
electron transfer and surface reorganization. Hence, in water oxidation research involving metal phosphides, sulfides, and other non-metal oxides, it is crucial to carefully account for the influence of the material's self-oxidation process when determining the active sites and the overall catalytic performance.

**Single-atom catalysts (SACs).** Electro catalysts boasting the highest activity and stability are primarily based on noble metals, such as Pt, Ir, and Ru. However, their significant cost and rarity pose challenges. To this end, two approaches have been recognized: 1) exploring alternative catalysts based on non-noble metals and 2) reducing the quantity of noble metals used without sacrificing efficiency. During the catalytic process, reactions predominantly occur near the catalyst's surfaces or interfaces, where the reactants are absorbed and transformed into products that detach from the surface or interface. Therefore, theoretically, scaling down their dimensions to clusters or even isolated metal atoms can substantially enhance the atom utilization efficiency, potentially reaching up to 100%, like homogeneous molecular catalysts. In the last decade, thanks to advancements in catalyst preparation and characterization techniques, the concept of single-atomic site catalysts (SASCs), commonly termed single-atom catalysts (SACs), has been extensively investigated. When dispersed at the atomic level, SACs can function similarly to homogeneous catalysts, demonstrating enhanced activity and stability compared to their homogeneous counterparts. Analogous to the ligand-metal configuration in a homogeneous catalyst, SACs require anchoring to specific supports, like metal or carbon-based materials, owing to their high surface free energy and highly unsaturated characteristics.

Various SACs have been therefore developed for thermocatalytic reactions, organic catalytic reactions, photocatalytic reactions, as well as electrocatalytic reactions. Through the dedicated research, a range of synthetic methods and supports have been devised to fabricate efficient and robust SACs for catalytic applications. The SACs typically anchor on the vacancies, defects, or specific functional group sites on substrates, with single atoms coordinated by heteroatoms (N, O, S, P, etc.) in materials like metal oxides, carbides, nitrides, and graphene. Numerous synthetic techniques for SACs have been investigated, including wet-chemical synthesis, atomic-layer deposition, high-temperature pyrolysis, atom trapping, MOF-derived methods, electrodeposition, etc. Based on the mode of component integration, the controlled preparation of SACs can be broadly categorized into two primary strategies: the bottom-up approach and the top-down approach. For a detailed overview, one might consult certain reviews that offer a comprehensive exploration and introduction to specific
However, to date, the large-scale synthesis of high-loading SACs is still hindered by the high surface energy of individual metal atoms, which often leads to aggregation into clusters and nanoparticles.

The progress in characterization methods has enhanced the understanding of the formation mechanisms, coordination environments, and identification of atomically dispersed species, which are fundamental to the advancement of rapidly developed SACs. Advanced techniques, like atomic resolution scanning transmission electron microscopy and X-ray absorption spectroscopy, have been employed to investigate the electronic configuration and geometry of SACs. When combined with various in-situ/operando characterization techniques that monitor the atomic and structural features of catalysts during working conditions, provides crucial insights into dynamic structural evolution, active site identification, surface/interface intermediates interactions, and reaction pathways.

In recent years, several noble and non-noble metal-based SACs have been reported for electrochemical water oxidation. Especially, SACs based on 3d-transition metals, such as Co-loaded nitrogen-sulfur co-doped graphene oxide (Co-NSG), Co-trapped poly(heptazine imide) (PHI-Co), hetero-N-coordinated Co (HNC-Co), Co-doped TiO$_2$ nanorods (Co-TiO$_2$), and Fe, Co, and Ni anchored on N-doped, defect-rich graphene (M-NHGFs), have shown impressive water oxidation performance. Other examples include Mn site-immobilized N-doped graphene (Mn-NG), Ni@defective graphene, Ni-O coordinated on graphene-like carbon (Ni-O-G), and Fe$^{3+}$ anchored on ultrathin TiO$_2$ nanobelt (Fe-UTN). All these catalysts have exhibited remarkable water oxidation activity, achieving low overpotentials (<400 mV) under various pH conditions. Undoubtedly, recent studies have indicated that SACs possess significant activity; however, the origins of this activity remain a topic of debate. The overall heterogeneity, resulting from high-temperature pyrolysis, non-uniform support materials, and ambiguous active site structures/environment, limited their application in unraveling catalytic mechanisms. Therefore, catalytic systems capable of providing definitive coordination environments to facilitate the formation of structurally defined transition-metal active sites are essential for trustworthy mechanistic studies of heterogeneous OER. Nevertheless, the exceptional efficacy demonstrated by specific SACs, coupled with their significant potential for cost savings, makes them a promising system for further investigations.

**MOFs and M-COFs.** Molecular WOCs offer tunable structural and electrochemical properties, while inorganic material catalysts typically provide excellent catalytic stability and facilitate electrode fabrication. By
integrated characteristics of both molecular and inorganic catalysts, the development of organic-inorganic hybrid catalysts, where inorganic materials are modulated by organic ligands, has emerged as a burgeoning area in water oxidation catalysis research.

MOFs are structured porous materials constructed from metal nodes and organic ligands via coordination bonds. Similar to molecular catalysts, organic-inorganic hybrid MOFs possess well-defined, versatile chemical structures, diverse compositions, adaptable pore environments, and accessible active sites.\textsuperscript{197} Owing to their unique structural features, MOFs combine the benefits of both homogeneous and heterogeneous catalysts, offering vast potential for energy conversion and catalysis.\textsuperscript{198-201} MOFs are commonly employed as precursors to synthesis metal sites/clusters loaded carbon-based composites for electrocatalysis.\textsuperscript{202, 203} While progress has been made using this method, directly employing pristine MOF materials as electrocatalysts appears more promising by eliminating the need for pyrolysis treatment. Recently, substantial research has focused on optimizing MOFs to boost their OER activity and stability. Nonetheless, employing pristine MOFs directly as electrocatalysts for OER remains in the infancy stage. A series of monometallic MOFs, multi-metallic MOFs, 2D MOFs, metal-doped MOFs, and amorphous MOFs were synthesized and applied in water oxidation catalysis. A comprehensive overview of advancements in MOF-based WOCs is available.\textsuperscript{204} From the reported studies, a consensus has emerged that organic ligands significantly decrease the water oxidation potential of metal materials. Within organic-inorganic hybrid MOFs, coordinatively unsaturated metal sites have been pinpointed as the active centers for water oxidation catalysis.\textsuperscript{205-209}

In MOF-based WOCs, the coordination bonds are even less stable than ionic bonds in traditional inorganic materials; some degree of structural reconstruction of MOF-based catalysts may be unavoidable under test conditions. Specifically, carboxylic acid-based MOF and imidazole-based zeolitic imidazolate framework (ZIF) materials, despite their outstanding OER activities, tend to experience partial or complete structural reconstruction during the catalytic conditions.\textsuperscript{210-213} These changes often lead to the formation of highly active metal hydroxides or oxides, while the residual organic ligands could act as proton relays to promote water oxidation kinetics.\textsuperscript{214, 215} These unstable MOFs are typically viewed as precursors to the actual catalysts rather than being the true catalysts themselves. Hence, the in-situ characterization techniques and post-characterizing MOF materials after OER testing can track the dynamic evolutions during the catalytic process.
that are vital for understanding the active sites involved in their water oxidation processes.

COFs are also a class of ordered porous materials characterized by unique architectures with high surface areas and tunable pore structures, which can serve as frameworks to anchor and stabilize molecular metal sites, forming metalated COF (M-COF) catalysts with significant potential in electrocatalysis.\textsuperscript{216-219} Compared to MOFs, COF materials bonded by covalent bonds exhibit enhanced stability and resistance to both acidic and alkaline conditions by rational structural design. In contrast to carbon-supported SACs, COFs offer abundant, uniform, and distinctly periodic coordination environments, allowing for the creation of well-defined transition-metal active sites for reliable mechanistic studies of heterogeneous OER. The crystalline, ordered structures of COFs, coupled with their tunable open pores and distinct microenvironments, make COF-based molecular-site catalysts superior in catalytic performance and provide an optimal model for investigation of the reaction mechanism.

Given the harsh conditions of OER, only a few M-COF materials have been reported as WOCs to date. Kurungot and co-workers reported a Co\textsuperscript{2+} ions incorporated bipyridine-COF (Co-TpBpy).\textsuperscript{220} Under neutral pH conditions, Co-TpBpy shows an overpotential of 400 mV for OER to achieve a current density of 1.0 mA cm\textsuperscript{-2}. However, due to the Schiff-base nature of linkages, the catalyst is not stable under alkaline conditions. The Chen group presented a metalloporphyrin-based graphdiyne (Co-PDY) analog with Co-N\textsubscript{4} moieties for electrocatalytic OER.\textsuperscript{221} When employed as a working electrode in 1.0 M KOH electrolyte, Co-PDY/copper foam demonstrated good OER performance, requiring an overpotential of 270 mV to achieve a current density of 10 mA cm\textsuperscript{-2}. The diversity and customizability position M-COFs as promising candidates for water oxidation catalysis, even though the field is still in its early stages. Based on this concept, Chapter 4 reports a molecularly well-defined heterogeneous WOC with aza-fused, $\pi$-conjugated, microporous polymer (Aza-CMP) coordinated single cobalt sites (Aza-CMP-Co). The isolated cobalt sites with Co-N\textsubscript{2}O\textsubscript{4} moieties demonstrate exceptional activity and stability under alkaline and near-neutral conditions. The well-defined molecular nature makes Aza-CMP-Co a reliable model for investigating heterogeneous water oxidation mechanisms.

**Immobilized molecular WOCs.** Molecular catalysts can be anchored onto suitable electrodes for electrochemical water oxidation in heterogeneous systems. Over the last decade, various techniques have emerged to immobilize these molecular catalysts onto functional electrodes for heterogeneous reactions. Typically, these methods are categorized based on
the nature of the interaction between the molecular catalysts and the conductive substrate surfaces, including both physical and chemical attachments. Molecular catalysts functionalized electrodes via physical interactions primarily fall into two categories: 1) π-π, CH-π, or hydrophobic interactions between the polyaromatic or alkane chain substituents of catalysts and carbon substrates; 2) catalysts encapsulated within polymeric layers. A more stable attachment can be established by forming covalent bonds between catalysts and the electrode surface. Several synthetic procedures, including diazonium group reduction, alkyne-azide click reactions, and ester bond creation using pyridinic, carboxylic, and phosphatic groups, are utilized to covalently bind molecular catalysts to carbon-based electrodes or conductive metal oxides (Figure 23). Several recent reviews have extensively discussed the specific cases and the associated immobilization strategies. Most research on immobilized catalysts has centered on precious metal systems like Ru and Ir. Hence, there is an urgent need to channel efforts towards developing highly efficient and stable catalysts using non-noble metal elements, aiming to significantly reduce device costs.

1.3.4 Water oxidation mechanisms over heterogeneous systems

Heterogeneous catalytic reactions constitute approximately 90% of processes in the chemical industry. A thorough understanding of the physio-chemical aspects of catalytic processes is thus crucial for accurate devices/reactor modeling. The necessity of kinetic investigations in heterogeneous catalysis is closely connected to the challenges faced by the chemical industry, including optimizing the reactor design, assessing the side reactions, and understanding the impact of dynamic effects on device performance. Any industrial application thus starts from reaction kinetics and underscores the importance of understanding the reaction at a molecular level.

Fundamentals in heterogeneous electrocatalysis. Heterogeneous catalysts in practical applications come in diverse compositions, geometrical forms, and porosities. Therefore, the fundamentals of mass and energy transfer in heterogeneous catalysis are crucial for detailing the procedures involved in the following elementary steps, including diffusion, adsorption, surface reaction, and desorption (Figure 24a). The commonly employed approaches to address surface reactions, including the Langmuir-Hinshelwood mechanism and Eley-Rideal mechanism, which presume uniform surfaces that all surface sites are identical, and the binding energies of reactants remain consistent regardless of surface coverage, ignoring potential interactions between the adsorbed species. However, the intricacy of solid surfaces means that adsorbed species can form diverse complexes on various
potential active sites, such as steps, kinks, corners, and vacancies (Figure 24b). This complexity complicates adsorption/desorption kinetics, the subsequent identification of active sites, and the determination of catalytic reaction mechanisms. Furthermore, interfaces that involve charged surfaces and aqueous electrolytes are ubiquitous in electrochemical catalysis. The interdependence between the charged catalyst surface and water behaviors underscores the importance of understanding the interfacial structure. While the Gouy-Chapman-Stern model provides a classical depiction of the electrical double layer, this mean-field model falls short in describing non-ideal interfacial systems and the intricate phenomena observed in actual catalytic systems (Figure 24c). To address this challenge, a combination of in-situ, operando, time-resolved, and surface-specific measurements, complemented by simulations under non-equilibrium conditions, is essential.234

Figure 24. (a) General pathways for heterogeneous electrode reactions. (b) Schematic diagram illustrates the various sites on a metal oxide surface due to the presence of steps, kinks, corners, etc. Vacancies and other types of surface defects are not shown. The small blue dots represent metal cations, and the larger
red dots represent oxygen anions. The label NC represents the coordination number of N. Adapted with permission from reference 176, Copyright 2017, American Chemical Society. (c) Schematic description of the Gouy-Chapman-Stern model. Indicated are the inner Helmholtz plane (IHP), the outer Helmholtz plane (OHP), the thickness of the Stern layer, \( d \), and the thickness of the diffuse layer, also known as the Debye length, \( \kappa^{-1} \). The purple, green, and yellow spheres represent the cations, the anions, and neutral species, respectively. Adapted with permission from reference 234, Copyright 2021, Springer Nature.

As mentioned in the homogeneous WOC section, PCET is a critical step in water activation and O-O bond formation processes. In the homogeneous electrochemical PCET, the electrode acts merely as an electron reservoir, remaining inactive in the chemical reaction. Here, electron transfer occurs between the electrode and a redox molecule in solution (analogous to outer-sphere electron transfer), while PT takes place within the redox molecule or between it and another proton donor/acceptor (Figure 25a). However, in heterogeneous systems, the electrode not only serves as an electron reservoir but also plays an active role in forming and breaking chemical bonds (analogous to inner-sphere electron transfer). Here, protons either migrate towards or away from the electrode surface includes the electrode and any chemisorbed species (i.e., surface-bonded \( \text{H}_2\text{O}/\text{OH}^- \) in water oxidation reactions) (Figure 25b).

Figure 25. Schematic illustrations of (a) homogeneous and (b) heterogeneous electrochemical PCET. Schematic (c) outer-sphere and (d) interfacial \( 1\text{H}^+/1\text{e}^- \) PCET steps.
Figure 25c presents the outer-sphere $1\text{H}^+/1\text{e}^-$ PCET steps in homogeneous electrochemical reactions. The PCET can proceed through three energetically equivalent pathways: the CPET process directly transforms reactant $1\text{a}$ into product $2\text{b}$; the sequential processes entail charged reaction intermediates, transitioning from $1\text{a} \rightarrow 1\text{b} \rightarrow 2\text{b}$ (PTET) or $1\text{a} \rightarrow 2\text{a} \rightarrow 2\text{b}$ (ETPT). Compared to the CPET process, the sequential transition is more straightforward, essentially representing the combination of individual PT and ET in a stepwise process. From a thermodynamic perspective, the Gibbs free energy change ($\Delta G$) for CPET is always more negative than for singular ET or PT (Figure 26a). This is evident because sequential processes must go through an intermediate that transfers only a proton or an electron. The energy of this intermediate is inevitably higher than that of the product; otherwise, it would become the final product. While a concerted mechanism is undeniably more favored thermodynamically, it is pivotal to recognize that thermodynamics does not determine the actual mechanism, as the reaction rate is directly related to the kinetics corresponding to the energy barrier.

Figure 26. (a) Diabatic (blue) and adiabatic (red) electronic states as functions of the proton coordinate. The $x$ coordinate is the proton transfer coordinate, and the $y$ coordinate is the electron energy. Adapted with permission from reference 235, Copyright 2008, American Chemical Society. (b) Schematic illustrations of the electrochemical PCET processes on different surface species.

The aforementioned insights into outer-sphere PCET mechanisms become less applicable for heterogeneous electrochemical PCET. Due to the extended band structure in metals, the charge gets entirely delocalized across the metal, making both the stepwise PTET and ETPT pathways infeasible (Figure 25d). As the charge from the proton disperses instantly due to delocalization, ET cannot occur separately without the formation or cleavage of surface bonds (i.e., PT). While this might be accurate for hydrides (M-H),
where hydrogen directly bonds with the metal surface, it is not necessarily the case for the key intermediate M-OOH during water oxidation (Figure 26b). Here, electron transfer often depends on the redox-active oxygen(s) or metal site(s), with variable valence states and localized electrons, which implies that the PCET process on the M-OOH surface species might not be simply concerted. Indeed, decoupled PCET processes have been widely observed in the RDS of material WOCs with pH-dependent activity. Also, for immobilized molecular systems, where there is a significant distance between the surface and transferred proton, cases with decoupled PCET processes have been noted for metal redox processes, challenging the conventional interfacial PCET theory framed by the Volmer reaction. The PCET features are intrinsically linked to the electronic structure of the electron donor/acceptor. Consequently, the structural connection and the proximity between the proton transfer site and the electrode surface, essentially the surface configuration of catalysts, play pivotal roles. Furthermore, whether in homogeneous or heterogeneous systems, the PT process is deeply related to the properties of the proton donor/acceptor, making the solvent structure at the interface vital in guiding the electrochemical PCET procedure. At present, the boundary between outer-sphere electrochemical PCET and interfacial PCET remains ambiguous (Figure 26b). Specifically, there is a notable absence of specific descriptions concerning the interface model of key intermediates in water oxidation, which highlights the need for a well-defined surface model to enable more precise molecular-level studies.

To address the rate of the PT process ($k^{PT}$), the most straightforward approach is to directly employ transition state theory (TST) without considering the hydrogen tunneling effects:

$$k^{PT}_{TST} = \frac{k_B T}{\hbar}\exp\left(-\frac{\Delta G^\ddagger}{RT}\right) \quad (14)$$

Where $k_B$ is the Boltzmann constant, $\hbar$ is the Planck constant, $T$ is thermodynamic temperature, $\Delta G^\ddagger$ is the reaction activation energy. Discussions on ET rates ($k^{ET}$) are primarily within the framework of Marcus theory. Under nonadiabatic electron transfer conditions, the rate for an anodic reaction can be expressed as follows:

$$k^{ET}_a(\eta) = \frac{(V_{el})^2}{\hbar} \frac{\pi}{k_B T \lambda} \rho_M \int [1 - f(\epsilon)] \exp\left[-\frac{(\epsilon - e\eta + \lambda)^2}{4k_B T \lambda}\right]d\epsilon \quad (15)$$

Where $V_{el}$ is electronic coupling, $\lambda$ is reorganization energy, $\eta$ is overpotential, $\hbar$ is reduced Planck constant, $f(\epsilon)$ is the Fermi distribution function for the
electronic states in the electrode, $\rho_M$ is the density of states at the Fermi level, which is assumed to be a constant. Very similar to the Marcus type ET process, the nonadiabatic, anodic heterogeneous PCET rate constant ($k^{\text{PCET}}$) over the distance $R$ between the proton acceptor and the electrode surface can be written as:

$$k^{\text{PCET}}(R, E) = \frac{\rho_F}{\hbar} \sqrt{\frac{\pi}{k_B T \lambda}} \sum_{\mu, \nu} P_\mu |V_{\mu\nu}(R)|^2 \int [1 - f(\epsilon)] \exp \left[ - \frac{(-\Delta G_{\mu\nu}(R, E, \epsilon) + \lambda)^2}{4 k_B T \lambda} \right] d\epsilon \quad (16)$$

Where $\rho_F$ is the density of states at the Fermi level for the electrode, $\lambda$ is the total reorganization energy, $P_\mu$ is the Boltzmann population of the reactant vibronic state $\mu$, $V_{\mu\nu}(R)$ is the coupling between the vibronic states $\mu$ and $\nu$, and $f(\epsilon)$ is the Fermi distribution function. The free energy difference $\Delta G_{\mu\nu}(R, E, \epsilon)$ for the pair of states $\mu$ and $\nu$ depends on the distance $R$ to the electrode surface, the applied potential $E$ relative to the reference potential, and the energy of the electronic level $\epsilon$ relative to the Fermi level. The detailed derivations can be found in the literature.$^{247, 248}$

To summarize, the rate constant for ET can be determined by evaluating the reorganization energy, electronic coupling, and density of states at the Fermi level. The rate constant for PT is derived from the free energy barrier. For CPET, the rate constant is ascertained by assessing the reorganization energy, electronic coupling, density of states at the Fermi level, free energy change, and Boltzmann population. Generally, given the complex reactions associated with CPET, its energy barrier tends to be higher than that of straightforward ET or PT. This suggests that CPET, while thermodynamically favorable, presents kinetic challenges, underscoring the complexity of the PCET mechanism. After determining the rate constants for PT, ET, and CPET reactions across various species, combined with the determination of redox potential and $pK_a$ of surface species, one can employ microkinetic modeling to analyze the interrelationships among the different mechanisms for homogeneous HER,$^{249}$ heterogeneous HER,$^{250}$ heterogeneous ORR,$^{251, 252}$ and heterogeneous NO electroreduction.$^{253}$ However, its application in OER mechanism screening remains limited, probably due to the complex deprotonation nature between two water molecules.

Heterogeneous catalysis at the electrode-solvent interface offers diverse chemical possibilities, incorporating both surface atoms and solvated molecules. Mechanistic explorations of such catalysts face challenges, primarily due to inadequate experimental characterizations and
computational intricacies, especially from interfacial effects and defects. In actual experiments, discerning the PCET mechanism poses challenges. However, it can still be discerned through thermodynamic exclusionary arguments, assessments of kinetic isotope effects (KIEs), temperature dependency, driving force dependency, and other methods.\textsuperscript{71} In computational explorations, the precision and applicability of theoretical methods for heterogeneous catalysis lag behind those for molecular electrocatalysts. Nevertheless, ongoing advancements in both theoretical and experimental techniques are shedding light on the catalytic characteristics of heterogeneous catalysts. Employing a hybrid material of molecular and heterogeneous catalysis may be the most effective approach to harnessing renewable energy for prevailing energy issues.

**Heterogeneous water oxidation reaction pathways.** The complexity of catalyst surfaces in materials has made the heterogeneous water oxidation mechanism a contentious topic. Nonetheless, three primary reaction pathways with different O-O bond formation processes have been recognized to elucidate the pivotal steps in water oxidation: adsorbate evolution mechanism (AEM), lattice oxygen mechanism (LOM), and oxygen coupling mechanism (OCM). Generally, such reaction pathways for heterogeneous water oxidation closely resemble that of homogeneous catalysis and can also be treated as four key processes, including water binding, water activation, O-O bond formation, and oxygen release.

The AEM is proposed to proceed through four PCET reactions (Figure 27a). First, water is chemisorbed onto the coordinatively unsaturated site (water binding) and then undergoes deprotonations to generate M-OH and M=O/M-O* species across two oxidation steps (water activation). Subsequently, the O-O bond is formed through an APT-controlled water nucleophilic attack, resulting in an M-OOH intermediate (O-O bond formation). Finally, the O\textsubscript{2} molecule desorbs from the catalyst surface, accompanied by the last deprotonation process, releasing the active metal site and looping the reaction (oxygen release). Alternatively, the OCM route couples the neighboring adsorbates directly to deliver the O-O bond formation, which analogue of I2M pathways in the homogeneous system (Figure 27e). Specifically, this coupling can theoretically occur between two M=O/M-O* entities,\textsuperscript{254} two M-OH entities, or a combination of one M-OH and one M=O/M-O* species.\textsuperscript{255} In AEM and OCM, the catalyst interface is theorized to remain stable, with only the valence state of the metal center altering during oxygen evolution.
In contrast, the LOM suggests that the catalytic interface is no longer thermodynamically stable and undergoes dynamic changes accompanying the exchange and release of lattice oxygen ligands throughout the oxygen evolution process. Lattice oxygen activation is a prerequisite to trigger the LOM pathways, necessitating unique electronic structures in the catalyst. The
O-O bond formation in LOM can arise between a lattice oxygen and an adsorbed oxygen or between two lattice oxygens. Depending on the number of lattice oxygens involved and their bonding modes, LOM can be further categorized into three types: single site, dual site, and vacancy site. In LOM via vacancy site, the activated lattice oxygen can readily act as an active site for water nucleophilic attack from solutions to form M-OOH species (Figure 27b).242 The release of the O₂ generates an oxygen vacancy site, which is refilled by H₂O/OH⁻ in the subsequent catalytic cycle. In the single-site LOM mechanism, surface reconstruction enables directly coupling one activated water intermediate (M=O/ M-O•) with one activated lattice oxygen (Figure 27c).237, 256 The resultant M-OO species releases oxygen in a manner similar to the I2M mechanism, completing the catalytic cycle. In the dual-sites LOM mechanism, the intramolecular coupling of adjacent activated lattice oxygens results in a peroxo-like M-OO-M moiety (Figure 27d).257, 258 This is followed by O₂ release and the replenishment of two lattice vacancy sites with solvent molecules. In fact, the homogeneous water oxidation mechanism can adequately illustrate the O-O bond formation mechanism in heterogeneous systems (Figure 27f). The O-O bond formation in AEM and vacancy site-mediated LOM aligns with the WNA mechanism. The formation in single-site-mediated LOM parallels the IOC process, while the process in dual-site-mediated LOM is analogous to the RI process. Lastly, the O-O bond formation in OCM mirrors the i-I2M process. This classification reaffirms that research on the catalytic mechanism using homogeneous WOCs offers valuable insights for heterogeneous systems.

The cleavage of the O-H bond is an endothermic process, given the bond dissociation energy of the H-OH bond reaches a substantial 118 kcal mol⁻¹. As a result, activating the O-H bond, especially when linked with O-O bond formation presents a significant challenge. If the interfacial proton transfer no longer dictates the reaction rate, a faster reaction rate might be achievable. In other words, OCM and LOM involving the oxygen coupling process could exhibit faster kinetics than the conventional AEM characterized by a diffusion-controlled interfacial atom-proton transfer process.

**Structure-mechanism relationship.** The AEM is typically assumed to involve four CPET reactions centered on the metal ion, producing *OH, *OOH, and *O intermediates (* represent surface sites). Given the linear correlation between the binding energies of these intermediates, descriptors linked to the adsorption energy seem promising for predicting activity trends. An optimal catalyst exhibits oxygen binding that is balanced – neither too strong nor too weak – resulting in a (ΔG₀* – ΔG_HO*) of 1.6 eV (Figure 28a).259 By modifying the electronic structure, particularly through methods,
such as elemental substitution, vacancy creation, strain adjustment and interface engineering, it is possible to achieve a highly active catalyst.\textsuperscript{260} Significant research has focused on pinpointing the surface electronic structure, which corresponds to the binding energy of oxygen species on surfaces and can be used as a potential descriptor for describing the structure-activity relationship. For instance, in the case of perovskites, the $e_g$ occupancy of the 3$d$ electron can act as an activity descriptor; optimal OER activity is achieved when the $e_g$ occupancy approaches one (Figure 28b).\textsuperscript{261} It is worth noting that, in such approaches, identifying the step with the highest Gibbs free energy as the RDS might be misleading. While a process may be thermodynamically favorable, it does not guarantee that it is kinetically favorable. As previously mentioned, while thermodynamically advantageous, the complicated PCET process poses kinetic challenges.

![Figure 28](image)

**Figure 28.** (a) Volcano plot of the calculated activities trends against descriptor ($\Delta G_{O^\bullet} - \Delta G_{H^\bullet}$) for various metal oxides; adapted with permission from reference 259, Copyright 2011, Wiley-VCH. (b) Relation between OER activity and $e_g$ occupancy of transition metal cations (B in ABO$_3$); adapted with permission from reference 261, Copyright 2011, American Association for the Advancement of Science.

As previously highlighted, effectively activating the O-H bond in water and accelerating the interfacial proton transfer in the RDS emerges as a worthy direction for designing superior material-based WOCs. Recently, in-depth mechanistic studies suggest that when proton transfer is involved in the RDS, integrating proton acceptors, such as carboxylate\textsuperscript{214} or sulfonate\textsuperscript{262} groups, proximal to the catalytic centers can facilitate proton transfer and water oxidation kinetics (Figure 29). These insights imply that enhancing the interfacial proton transfer of the RDS in the AEM process via outer-sphere modifications can boost a catalyst's performance.
The intrinsic relationship between the electronic structure of catalysts and OER mechanisms can also be elucidated by metal-oxygen covalency using molecular orbital theory. Taking the octahedral MO₆ motif for illustration, the orbital interaction and band diagram can be depicted in Figures 30a and 30b. The band structure of transition-metal oxides simply considers the orbital overlaps between the transition-metal d orbitals and the oxygen p orbitals. This results in the formation of bonding (M-O) and antibonding (M-O)* bands, characterized distinctly by their strong ligand and metal properties, respectively (Figure 30c). The energy gap between (M-O) and (M-O)*, referred to as the charge transfer term $\Delta$. This charge transfer term signifies the ionic-covalent nature of the M-O bonds, and a reduced value suggests increased hybridization, emphasizing the augmented covalency of the M-O bond. The Coulomb interaction within the d orbitals induces the inherent electron repulsion. Consequently, the term $U$ is used to describe the energy difference between the empty upper Hubbard band (UHB) and the filled lower Hubbard band (LHB) in Mott-Hubbard splitting. The position of LHB with respect to the (M-O) band thus depends on the relative values of $U$ vs. $\Delta$, giving rise to three distinct situations with different water oxidation mechanisms. For the case where $U \ll \Delta$, a scenario commonly observed in oxides characterized by highly ionic M-L bonds (L = ligand), the O 2p band is positioned deep within the energy diagram, while the M nd band is located above (Figure 30d). Thermodynamically, electron transfer should occur between the metal center (cationic M redox) and adsorbed oxygen intermediates, facilitating the OER reaction through the conventional AEM pathway.
Figure 30. (a) The molecular orbitals and (b) band energy diagram for octahedral MO₆. (c) The schematic band structure of transition-metal oxides. (d-f) The schematic representations of cation(M)/anion(O) redox chemistry guided by d-d Coulomb interaction term U and the charge transfer term Δ. The relationship between the OER mechanism and electronic descriptors for Co-based (g) perovskite and (h) spinel oxide electrocatalysts; adapted with permission from reference 265, Copyright 2021, Royal Society of Chemistry.

As the charge transfer energy decreases and $U$ increases, the adjusted electronic band allows the LHB to overlap with the O 2p band. Consequently, intramolecular electron transfer from oxygen ligands to transition metal
cations (positively charged lattice O ligands) within the lattice becomes viable, setting the foundation for lattice oxygen activation (Figure 30e). In this context, enhanced metal-oxygen covalency facilitates improved charge transfer between the active sites and adsorbates, which lowers the energy barrier, promoting water nucleophilic attack.\textsuperscript{266, 267} It is noteworthy that this scenario resembles the introduction of negatively charged groups (\(\sigma, \pi\)-donation) to the ligands of molecular WOCs, which significantly reduces the redox potential for the water activation process. When \(U >> \Delta\), the redox process continues, but with electrons being directly extracted from the O 2\(p\) band positioned above the filled LHB (anionic O redox) (Figure 30f). These conditions might generate highly reactive O\(^{\text{v-}}\) species, which could de-coordinate from the metal lattice either via reductive elimination or by attacking the electrolyte, i.e., LOM. The inverse arrangement of M nd and O 2\(p\) bands can be notably accomplished by elevating the oxidation states of late transition metal centers, which aligns with the understanding that high-valence metal species in molecular WOCs can activate water molecules, producing highly reactive M=O/M -O• species. In summary, the energy alignment between M nd (\(\varepsilon_{\text{M nd}}\)) and O 2\(p\) (\(\varepsilon_{\text{O 2p}}\)) bands, along with the absolute energy level of the O 2\(p\) band, significantly influence the OER mechanism. A negative \(\varepsilon_{\text{M nd}} - \varepsilon_{\text{O 2p}}\) and high \(\varepsilon_{\text{O 2p}}\) values would trigger LOM, which is also supported by the comprehensive computational analysis of perovskite (Figure 30g) and spinel (Figure 30h) oxides WOCs.\textsuperscript{242, 268}

For successful lattice oxygen activation in LOM, the electronic structures of WOCs need to be strategically modified to increase the covalency of the M-O bond (Figure 31a). Consider a metal oxide with the formula A\(_x\)M\(_y\)O\(_z\), where A represents a non-active metal cation, and M signifies a catalytically active metal cation. Enhancing the covalency of the M-O bond can be accomplished through three main methods: 1) reducing the band energy of M-sites, 2) elevating the energy of O-sites, and 3) incorporating the non-bonding O state (Figure 31b). Following such guidelines, substituting the A-site with metals of a lower oxidation state,\textsuperscript{256, 269} inducing A-site cationic deficiency,\textsuperscript{267, 270} or direct M-site cationic substitution\textsuperscript{271, 272} can adeptly modulate the valence states of both M cations and oxygen ligands. This results in an increased valence of the M-site cation and the introduction of ligand holes into the oxygen ligand, enhancing the M-O covalency. Consequently, the LOM pathway with lattice oxygen oxidation becomes more energetically viable. Furthermore, creating oxygen vacancies in the lattice matrix can significantly enhance lattice oxygen redox chemistry by effectively adjusting the relative positions of the M nd and O 2\(p\) bands.\textsuperscript{273-275} These oxygen defects can also work as lattice vacancy sites, adsorbing H\(_2\)O/OH\(^{-}\) for subsequent catalytic cycles. Besides, incorporating the non-bonding O 2\(p\) band, positioned
between the bonding (M-O) and antibonding (M–O)* bands, into the WOCs provides an opportunity to activate LOM without substantially altering the M
\[ n \rightarrow O \ 2p \] orbital hybridization.\(^{237}\)

**Figure 31.** (a) Schematic diagram of ionicity and covalency in molecular orbitals. (b) Approaches for exploiting LOM-induced WOCs, illustrated using molecular orbitals.

**Perspective.** The descriptors provide predictive frameworks for water oxidation mechanisms in crystallized materials, although many of them are specific and only applicable to certain groups of materials, leading to frequent mismatches between theoretical predictions and experimental outcomes. The comprehension of the water oxidation mechanism and its structure-activity relationship remains challenging. It is widely acknowledged that adjacent active sites can enhance their catalytic activity through a synergistic effect. Yet, the precise mechanism remains elusive, which requires further experimental and theoretical investigations.\(^{195, 276, 277}\) Detecting and differentiating the real-time formation of reactive intermediates and tracking the dynamic evolution of catalysts to offer insights into intermediate behaviors remains a challenge, which underscores the need for further advancement in **operando** spectroscopic and probe techniques.\(^{278, 279}\) Moreover, a profound theoretical understanding of heterogeneous PCET, the associated APT process, and the development of proton-related experimental methodologies (KIE, pH dependency, proton inventory, etc.)
specifically for water oxidation remains in the initial phases. Beyond that, the presence of diverse catalytic sites within a single heterogeneous catalyst complicates mechanism investigations. For example, the intricate, disordered, and unpredictable chemical environments in amorphous materials suggest multifaceted catalytic processes. Additionally, aspects such as phase segregation, defect states, and facet effects introduce multiple potential catalytic pathways in crystalline materials. These mixed mechanisms in a single reaction system complicate the interpretation and assignment of experimental kinetic results. In addition, while significant advancements have been made in developing various support materials for anchoring isolated catalytic sites, most of these support materials exhibit non-uniform characteristics, creating diverse chemical environments around the metal atoms. The overall heterogeneity of these catalytic sites, even if the catalyst is stable, limits their utility in detailed catalytic mechanism investigations. Regrettably, comprehensive, in-depth mechanism studies on these immobilized metal sites remain scarce; they still offer the possibility of understanding heterogeneous water oxidation catalysis at a molecular level.

1.4 Light-absorbing materials

The arena of PEC-driven solar fuel generation, particularly water splitting, began with the groundbreaking discovery of water electrochemical photolysis using semiconducting TiO$_2$ in 1968. Subsequently, Fujishima and Honda introduced the idea of utilizing an n-type semiconductor within the PEC cell framework. To date, extensive research has explored various semiconducting materials, leading to the discovery of several promising PEC photoelectrodes and deepening insights into their inherent properties and operational mechanisms. Owing to the complexities of multiple electron and proton transfers in water oxidation, crafting efficient and durable photoanodes becomes vital for producing PEC devices with improved STH conversion efficiency. This thesis aims to advance existing photoanode materials and explore new candidates for highly efficient PEC water splitting.

1.4.1 Approaches to efficient photoelectrodes

The selection of appropriate light-absorbing materials, which can simultaneously generate sufficient photovoltage and effectively harvest a large portion of the solar spectrum, is crucial for PEC water splitting. An optimal light-absorbing material should fulfill the following principal requirements:

(1) Proper band gap and energy band positions.
(2) Efficient charge transport properties.
(3) Good operational stability.
Earth-abundant, non-toxic, low-cost, and scalable. This section will discuss in detail the influencing factors of these requirements.

**Band gap and energy band positions.** From a thermodynamic perspective concerning water splitting reaction, successful overall water splitting demands that the conduction band minimum (CBM) of the semiconductors is situated at a potential more negative than the proton reduction potential (0 V vs. NHE at pH 0). Additionally, to effectively oxidize water, the valence band maximum (VBM) of the semiconductors should surpass the water oxidation potential (+1.23 V vs. NHE at pH 0). The theoretical 1.23 eV corresponds to the energy of a photon with a wavelength of approximately 1010 nm; around 75% of all solar photons are theoretically usable for water splitting ([Table 1](#) and [Figure 32](#)). The band gap of semiconductors must ensure significant solar spectrum absorption within such requirements to achieve an elevated theoretical $\eta_{STH}$. Specifically, the visible light spectrum, ranging 400-780 nm, constitutes 52% of total solar energy and is considered the optimal range for solar energy conversion, which necessitates the development of materials with a band gap ranging from 1.59 to 3.1 eV. As outlined in section 1.2.3, after comprehensively considering the substantial energy losses due to the Shockley-Queisser limit, reaction overpotential, and charge recombination, the water oxidation photoanode with a single absorber shows an optimal band gap of 2.26 eV, representing a maximum theoretical $\eta_{STH}$ of 11.2%. For double-junction absorbers (i.e., Z-scheme), the optimal band gaps range between 1.65-1.8 eV (top layer) and 0.95-1.15 eV (bottom layer), leading to a theoretical $\eta_{STH}$ surpassing 25%. Hence, identifying and advancing visible-light-absorbing semiconductor materials that possess the appropriate band gaps and energy band positions is pivotal to the ongoing progress in the PEC field.

**Table 1. Energy distribution in AM 1.5G solar spectrum.**

<table>
<thead>
<tr>
<th>Spectral region</th>
<th>Wavelength (nm)</th>
<th>Energy (eV)</th>
<th>Proportion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>near-UV</td>
<td>300-400</td>
<td>4.13-3.10</td>
<td>4.6</td>
</tr>
<tr>
<td>Purple-blue</td>
<td>400-485</td>
<td>3.10-2.56</td>
<td>11.7</td>
</tr>
<tr>
<td>Cyan-yellow</td>
<td>485-590</td>
<td>2.56-2.10</td>
<td>15.9</td>
</tr>
<tr>
<td>Orange-red</td>
<td>590-780</td>
<td>2.10-1.59</td>
<td>24.5</td>
</tr>
<tr>
<td>Near-IR</td>
<td>780-1010</td>
<td>1.59-1.23</td>
<td>18.1</td>
</tr>
<tr>
<td>Near-IR</td>
<td>1010-2500</td>
<td>1.23-0.5</td>
<td>24.5</td>
</tr>
</tbody>
</table>
In PEC water splitting involving redox reactions under aqueous conditions, the interface between the photoelectrode and the electrolyte is crucial. Figure 33 provides a detailed illustration of the band energetics at a semiconductor/electrolyte junction. For a typical n-type semiconductor, upon interfacing with the electrolyte, a thermodynamic equilibrium forms across the interface, leading to the creation of a depletion layer. Under light exposure, the quasi-Fermi level for electrons ($\mu E_F$) remains consistent with the equilibrium Fermi level ($E_F$), while the quasi-Fermi level for holes ($pE_F$) moves closer to the valence band edge. This shift in the quasi-Fermi level, known as the quasi-Fermi level splitting (QFLS), directly influences the photovoltage ($V_{ph}$). The flat-band potential ($E_{fb}$) of a semiconductor-electrolyte interface is the potential at which the energy bands of the semiconductor are flat at the interface, and there is no net movement of charge across the interface. When the potential applied to the photoanode is more cathodic than the flat-band potential, the transfer of photogenerated holes toward the semiconductor/electrolyte interface is forbidden due to the Schottky barrier. When the potential applied to the photoanode is more anodic than the flat-band potential, photogenerated holes will be attracted towards the semiconductor/electrolyte interface due to the downward band bending, where they can be possible to react with water molecules and contribute to the water oxidation reaction. Therefore, the position of flat-band potential determines the theoretical $E_{onset}$ of a photoanode. To be more detailed, if $pE_F$ is shallower than the thermodynamic potential required for water oxidation ($E_{OER}$), the water oxidation reaction still cannot occur due to the insufficient driving force. As a result, the $E_{onset}$ is more anodic than $E_{fb}$ (Figure 33a). On the other hand, when $pE_F$ is deeper than $E_{OER}$, OER will immediately occur when the applied potential exceeds $E_{fb}$ (Figure 33b).
Figure 33. Energy diagrams and schematic J-V curves for n-type semiconductor in contact with an aqueous electrolyte under different applied potentials: (a) $V_{ph}$ is smaller than the difference between $E_{OER}$ and $E_{fb}$. (b) $V_{ph}$ is larger than the difference between $E_{OER}$ and $E_{fb}$. 

**Figure 33.** Energy diagrams and schematic J-V curves for n-type semiconductor in contact with an aqueous electrolyte under different applied potentials: (a) $V_{ph}$ is smaller than the difference between $E_{OER}$ and $E_{fb}$. (b) $V_{ph}$ is larger than the difference between $E_{OER}$ and $E_{fb}$. 

**Figure 33**
In the semiconductor/electrolyte system, when NHE or RHE is used as the potential reference, $E_{fb}$ is the NHE/RHE potential corresponding to the Fermi level of the semiconductor in vacuum. Since the energy band level is an intrinsic property of the semiconductor given a certain fabrication procedure, the minimum $E_{onset}$ of the photoanode will not be shallower than the CBM of the semiconductor material. Therefore, to prepare a photoanode with a lower $E_{onset}$, the CBM of the semiconductor material should be more cathodic (i.e., higher value relative to the vacuum level) while ensuring sufficient photoelectrochemical voltage. In conclusion, taking an n-type single-junction absorber as an example, to achieve total water splitting without an external bias (i.e., $E_{onset} < 0$ V vs. RHE), the subsequent conditions must be fulfilled: 1) $E_F < 0$ V vs. RHE; 2) VBM $> 1.23$ V vs. RHE; 3) $V_{ph} > 1.23$ V.

**Charge transport properties.** Generally, the PEC water oxidation reaction performance is determined by three aspects: the optical response, carrier separation and transfer within the bulk of the semiconductor, and electrolyte/electrode interfacial carrier injection performances. These charge dynamics are deeply rooted in the intrinsic bulk and surface properties of photoelectrodes. As such, investigating the generation and separation of photo-induced carriers, along with associated modification approaches, is vital for enhancing the water oxidation performance of PECs.

Typically, the photocurrent density ($J_{ph}$) for the PEC water oxidation reaction can be described by the subsequent equation:

$$J_{ph} = J_{obs} \times \eta_{bulk} \times \eta_{surface} \quad (17)$$

Where $J_{obs}$ is the photocurrent density with the complete conversion of the incident photon, which is determined by the energy band structure and morphology of the photoelectrode; $\eta_{bulk}$ is the inner charge separation and transport efficiency within the material; $\eta_{surface}$ refers to the electrolyte/electrode interfacial carrier injection efficiency. The equation highlights that the photogenerated carriers undergo multiple recombination processes before reaching the photoanode interface for the reaction, leading to significant performance degradation. Therefore, to optimize the PEC water oxidation process, increasing the initial photo-induced carrier count and minimizing carrier recombination are of top importance.

The traditional Gärtner model gives $\eta_{bulk}$ in a semiconductor as below:

$$\eta_{bulk} = 1 - \frac{e^{-aW_D}}{1 + aL_p} \quad (18)$$
Where $L_p$ is the minority carrier (hole) diffusion length, and $\alpha$ is the absorption coefficient, $W_D$ is the width of the depletion layer. A broader $W_D$ and an extended $L_p$ are evidently beneficial for enhancing $\eta_{\text{bulk}}$. $W_D$ correlates with the applied potential and donor density ($N_D$) in the material, while $L_p$ is associated with the lifetime and mobility of holes. Therefore, enhancing the carriers' intrinsic properties through structural or compositional modifications is essential for $\eta_{\text{bulk}}$ improvement.

**Doping.** Doping is a prevalent approach in enhancing bulk charge transport by introducing shallow energy level dopant or delocalizing the polar metal-oxygen bond to increase the free carrier concentration as well as the conductivity of the semiconductor. Meanwhile, tuning the energy band positions and the gap can also be achieved by atomic doping. For n-type photoanodes, integrating n-type dopants (donor states) can enhance conductivity and boost charge separation/transfer efficiencies. For instance, elements such as W$^{6+}$ and Mo$^{6+}$, along with oxygen vacancies and interstitial hydrogen, have been demonstrated to be effective shallow donors for BiVO$_4$. Taking BiVO$_4$ as example, various materials have been explored to form heterojunctions with BiVO$_4$, including WO$_3$, SnO$_2$, TiO$_2$, ZnO, and Fe$_2$O$_3$. Notably, WO$_3$, with its aligned band positions, excellent electron mobility (around 10 cm$^2$ V$^{-1}$ S$^{-1}$), and significant diffusion length ($L_p$ close to 800 nm), stands out as the most successful pairing, resulting in highly efficient BiVO$_4$/WO$_3$ photoanodes. Heterojunctions of n/p-type have also been explored to enhance charge transport and broaden light absorption. This includes inorganic p-type semiconductors like Co$_3$O$_4$, NiO, LaFeO$_3$, etc., as well as organic semiconducting polymers, such as carbon nitrides and covalent triazine frameworks (CTFs).

**Heterojunction.** The efficiency of charge separation in light absorbers can be enhanced by establishing type II heterojunctions with other semiconductors by regulating the built-in electric field. Generally, an efficient n/n-type heterojunction should possess 1) good electron transfer properties, 2) a type II band alignment, and 3) a scaffold with a high porosity and specific surface area. Taking BiVO$_4$ as example, various materials have been explored to form heterojunctions with BiVO$_4$, including WO$_3$, SnO$_2$, TiO$_2$, ZnO, and Fe$_2$O$_3$. Notably, WO$_3$, with its aligned band positions, excellent electron mobility (around 10 cm$^2$ V$^{-1}$ S$^{-1}$), and significant diffusion length ($L_p$ close to 800 nm), stands out as the most successful pairing, resulting in highly efficient BiVO$_4$/WO$_3$ photoanodes. Heterojunctions of n/p-type have also been explored to enhance charge transport and broaden light absorption. This includes inorganic p-type semiconductors like Co$_3$O$_4$, NiO, LaFeO$_3$, etc., as well as organic semiconducting polymers, such as carbon nitrides and covalent triazine frameworks (CTFs).

**Low-dimension nanostructures.** In contrast to planar-structured photoanodes with poor interaction between electrode and electrolyte, semiconductor electrodes with designed nanostructures not only amplify their specific surface area but also enhance carrier transport and light-trapping capabilities. By crafting photoelectrodes with sophisticated 0D, 1D, and 2D nanostructures, carrier transport and interfacial injection processes are significantly improved due to minimized grain boundaries and reduced interactions.
charge transfer distances, leading to markedly water oxidation performances (Figure 34c). From this perspective, a variety of nanostructures, such as arrays of nanorods, nanowires, nanopillars, nanopyramids, nanosheets, nanotubes, and nanobowls, as well as inverse opal structures, network structures, hollow structures, and porous structures, have been investigated, which demonstrated to improve PEC performance significantly.  

![Figure 34](image)

**Figure 34.** (a) Potential locations of dopants for BiVO₄ lattice with monoclinic scheelite structure. (b) Schematics of BiVO₄/WO₃/fluorine-doped tin oxide (FTO) heterojunctions, hole transfer toward FTO, and recombination in the bulk of BiVO₄ were suppressed. Adapted with permission from reference 287, Copyright 2019, Wiley-VCH. (c) Illustration of photogenerated hole transport and interfacial carrier injection process of planar-structured polycrystalline, nanorod array, and nanobowl array. Adapted with permission from reference 310, Copyright 2021, Wiley-VCH.

Interfacial carrier recombination significantly limits the η_surface and hampers optimal PEC performance. At the electrolyte/semiconductor interface, three distinct charge distribution layers can be identified: the space charge layer (i.e., the depletion layer), the Helmholtz layer (or compact layer), and the Gouy layer (often referred to as the outer diffuse layer) (Figure 35a). Consequently, the potential drop across the double layer arises from three components: Δφ_SC in the space charge region, Δφ_H within the Helmholtz layer, and Δφ_G in the Gouy layer. In PEC processes, Δφ_G is often disregarded due to the high ionic concentration of the electrolyte. Surface states primarily arise from crystal lattice defects and adsorbed species within IHP. These states play a pivotal role in PEC activity, serving either as centers for recombination or as mediators for charge transfer. Therefore, the photoinduced charges, moving from the bulk phase to the surface redox agent, might undergo recombination either within the space charge layer (R_SC) or at
the surface state (RSS) (Figure 34b). Typically, $R_{SC}$ within the depletion layer is considered insignificant. Consequently, significant efforts have been directed toward minimizing surface recombination $R_{SS}$ losses to enhance $\eta_{surface}$.

Figure 35. (a) Potential and charge distribution across the electrode/electrolyte interface. Adapted with permission from reference 313, Copyright 2017, American Chemical Society. (b) Carrier transfer and recombination processes within photoanode. The pathways for carrier recombination include bulk recombination ($R_{bulk}$), space charge recombination ($R_{SC}$), and surface state recombination ($R_{SS}$).

Cocatalyst and surface overlayer. Pristine photoanode materials typically exhibit poor water oxidation kinetics, necessitating significant bias to drive the water oxidation reaction. Notably, enhancing semiconductor photoanode materials with cocatalysts has been demonstrated to effectively boost their interfacial water oxidation kinetics, leading to a more efficient carrier injection process and enhanced photocurrent density compared to unmodified semiconductors. The advancement in photo-electrocatalysis has been notably promoted by the discovery of robust electrocatalysts. Recently, various materials, such as metal oxides, metal (oxy)hydroxides, metal phosphates/phosphides, and metal-organic polymeric materials, have demonstrated their efficacy as cocatalysts layers to increase the photocurrent and reduce the current onset potential greatly.

While cocatalysts were initially developed to minimize the activation energy of water oxidation by offering a kinetically favorable pathway, their role is indeed rather complex. In fact, most successful modifications for $\text{BiVO}_4$ pertain to surface overlayers rather than being merely cocatalysts. The primary function of the cocatalyst is to reduce the activation energy, as evidenced by immobilizing molecular catalysts like Ru-based, Ir-based, or Co-based WOCs on $\text{BiVO}_4$. However, inorganic cocatalysts serve purposes beyond just accelerating catalytic kinetics, which also acts to
passivate surface states, preventing recombination on the semiconductor surface, essentially serving as protective or hole conductive/storage layers (Figure 36). The specific functions of cocatalysts/surface overlayers on photoanode surfaces can be analyzed using advanced electrochemical methods such as intensity modulated photocurrent spectroscopy (IMPS).\textsuperscript{340} For instance, using IMPS, Co-Pi was discovered to serve more as a passivation layer, reducing surface recombination, rather than as a catalytic layer to boost water oxidation kinetics.\textsuperscript{341} Additionally, spectroscopic techniques like transient absorption spectroscopy and photoinduced absorption spectroscopy offer further insights.\textsuperscript{342}

![Figure 36. Functions of surface overlayer on BiVO$_4$. Adapted with permission from reference 287, Copyright 2019, Wiley-VCH.](image)

**Electrolyte.** As highlighted in the WOC section, the electrolyte plays a pivotal role in influencing surface catalysis. Analogous to electrocatalytic water oxidation, alterations in electrolyte cations,\textsuperscript{343} anions (buffers),\textsuperscript{344} or pH\textsuperscript{345} within the PEC system can significantly modify the solvation of the reactant and the interfacial structure, thereby influencing the kinetics and stability of the surface reaction. For instance, the chemisorption of borate species accelerates water oxidation kinetics and minimizes surface recombination by trapping surface states on BiVO$_4$;\textsuperscript{346} Cs$^+$ species at the photoanode-electrolyte interfaces prevented further photo-corrosion of BiVO$_4$ and also promoted surface charge transfer and water oxidation;\textsuperscript{347} the presence of V$^{5+}$ species in the electrolyte prevents the photo-corrosion of BiVO$_4$ by inhibiting the photo-dissolution of V$^{5+}$ and also enhances water-oxidation kinetics by resulting in the formation of a vanadium-rich interfacial layer.\textsuperscript{348} While not as widely recognized as other methods, understanding the
roles of electrolyte ions remains crucial for surface catalysis. This insight suggests an innovative strategy to enhance surface kinetics in PEC systems by tailoring the electrolyte composition.

1.4.2 The current state of photoanodes

Light-absorbing materials in photoelectrodes can be categorized into PV-grade materials (e.g., Si, III-V semiconductors, and chalcogenides) and non-PV grade semiconductors (e.g., metal oxides, transition metal (oxy)nitrides, and carbon-based materials). PV-grade materials are typically well-crystallized with minimal defects and lattice mismatches, resulting in reduced bulk recombination. Many exhibit high carrier mobility, conferring excellent charge transport properties in associated PV devices. However, these PV-grade materials often lack resistance to photo-oxidation and corrosion in aqueous solutions, compromising their stability during prolonged water splitting operations. In contrast, non-PV-grade semiconductors, especially metal oxides, offer enhanced durability against photo-corrosion. Nonetheless, their intrinsic optoelectronic properties, such as carrier mobility and diffusion length, are generally much inferior to those of PV-grade materials. Single-junction PEC cells, even those using wide band gap materials, face high onset potentials due to complex water oxidation processes. Engineering an ideal semiconductor that combines stability, affordability, optimal band structures, high charge carrier mobility, and high absorption coefficient remains a challenge. To enhance the performance of the photoelectrode with different materials, there are primarily two strategies: 1) enhancing the efficiency of stable (oxides) materials, and 2) stabilizing high efficiency, low durability PV-grade materials.

![Figure 37. Band positions of typical PEC semiconductors in the pH 0 aqueous electrolyte compared with the energy potential for water splitting reaction. Red = valence band edge; blue = conduction band edge.](image)
Enhancing the efficiency of stable materials. The energy band structure of various semiconductors utilized in PEC applications is presented in Figure 37. Materials with wide band gaps, such as TiO$_2$ and ZnO$_2$, have restricted PEC utility because of their confined absorption spectrum. Nitrides and chalcogenides, exemplified by CdS and TaON, are prone to decomposition during water oxidation, rendering them impractical for use. PV materials, like Si, GaAs, and InP, have stability and cost concerns, diminishing their appeal as optimal choices. Metal oxide-based photoelectrodes responsive to visible light are favored for their affordability, ready availability, and inherent stability, making them the most researched materials for PEC water splitting.

![Figure 38. (a) Theoretical photocurrent density ($J_{\text{abs}}$) and STH efficiency of TiO$_2$, WO$_3$, Fe$_2$O$_3$, and BiVO$_4$ under one-sun irradiation. (b) Reported photocurrent density of metal oxide photoanodes under simulated one-sun for water oxidation. Adapted with permission from reference 287, Copyright 2019, Wiley-VCH.](image)

Visible light semiconductors, such as BiVO$_4$, Fe$_2$O$_3$, and WO$_3$, are currently the most used n-type semiconductors. Their band gaps, 2.7 eV for WO$_3$, 2.4 eV for BiVO$_4$, and 2.2 eV for Fe$_2$O$_3$, correspond to the light absorption cut-off edges of roughly 460 nm, 520 nm, and 560 nm, respectively. The narrow visible light absorption characteristics for WO$_3$ limit the improvement of its water oxidation photoanode performance. Both BiVO$_4$ and Fe$_2$O$_3$ offer...
broader light absorption. Under the standard AM 1.5G spectrum, their theoretical maximum photocurrents stand at 7.4 mA cm\(^{-2}\) for BiVO\(_4\) and 10.5 mA cm\(^{-2}\) for Fe\(_2\)O\(_3\), respectively (Figure 38a). BiVO\(_4\) exhibits rapid bulk carrier transfer, with its water oxidation photoanode devices in near-neutral electrolytes achieving photocatalytic current densities surpassing 6 mA cm\(^{-2}\), nearing its theoretical peak (Figure 38b). Conversely, Fe\(_2\)O\(_3\) photoanodes are hindered by poor bulk conductivity, suggesting a need for further enhancement in its water oxidation performance. The following part will provide a concise overview of the advancements in photoanode with promising BiVO\(_4\) and Fe\(_2\)O\(_3\) light-absorbing layers.

**BiVO\(_4\)**. Among the three polymorphs of BiVO\(_4\), including monoclinic scheelite, tetragonal scheelite, and tetragonal zircon, the monoclinic scheelite structure exhibits the highest photoactivity.\(^{350,\ 351}\) Monoclinic BiVO\(_4\) possesses a band gap ranging between 2.4-2.5 eV, which delivers a vivid yellow color. The CB primarily consists of V 3\(d\) states, with contributions from Bi 6\(p\) and O 2\(p\) contributions, whereas the VB is formed from hybridized orbitals of Bi 6\(s\) and O 2\(p\) states.\(^{352,\ 353}\) In BiVO\(_4\), the effective masses of photogenerated electrons and holes are 0.9m\(_0\) and 0.7m\(_0\), respectively (m\(_0\) denotes the electron's rest mass, equivalent to 9.11 × 10\(^{-31}\) kg).\(^{354}\) This low effective mass greatly facilitates the separation and transport of photogenerated carriers. The electron mobility of BiVO\(_4\) ranges from 0.02-0.044 cm\(^2\) V\(^{-1}\) s\(^{-1}\), with hole mobility at 2 cm\(^2\) V\(^{-1}\) s\(^{-1}\).\(^{287,\ 355}\) The limited electron mobility in BiVO\(_4\) is attributed to the imperfect overlap between the Bi 6\(p\) and V 3\(d\) orbitals in the CBM. The material has a moderate hole diffusion length of approximately 70-100 nm and a carrier lifetime of 40 ns.\(^{356}\) These distinctive attributes of BiVO\(_4\) have motivated extensive research aiming to harness its considerable potential in PEC cells.

When using pristine BiVO\(_4\) as a photoanode for PEC water splitting, the observed PEC performance often falls short of the expectations, primarily attributed to its sluggish carrier transport dynamics, severe surface recombination, and slow water oxidation kinetics. To address these challenges, numerous strategies have been innovatively proposed, drawing from key insights discussed in the preceding sections.\(^{287,\ 357}\) According to a recent review by Chi and co-workers (2022),\(^{32}\) the best catalyst-modified single-junction BiVO\(_4\) photoanode achieves a notable photocurrent density of approximately 6.4 mA cm\(^{-2}\) at 1.23 V vs. RHE while exhibiting good stability (Figure 39).\(^{358}\) Similarly, the best catalyst-modified multi-junction BiVO\(_4\)/WO\(_3\) photoanodes have been shown to achieve a photocurrent density surpassing 6.7 mA cm\(^{-2}\) at the same potential.\(^{359}\) Besides, the catalyst-modified Mo:BiVO\(_4\) photoanode already makes breakthrough stability over
Given the rise of highly efficient and stable BiVO$_4$-based photoanodes, the subsequent move is to incorporate these components into practical PEC systems for unassisted solar hydrogen generation.

**Figure 39.** Performance summary of BiVO$_4$-based photoanodes modified with different strategies. Adapted with permission from reference 32, Copyright 2022, Elsevier.

Fe$_2$O$_3$. Iron oxide (Fe$_2$O$_3$) manifests in both amorphous and crystalline forms, with the latter including the polymorphs $\alpha$, $\beta$, $\gamma$, and $\epsilon$. Among these, crystalline $\alpha$-Fe$_2$O$_3$, also known as hematite, is thermodynamically the most stable and most common oxide form with a red-brown color. The CBM of pure Fe$_2$O$_3$ is primarily characterized by localized Fe 3$d$ states; the VBM consists of Fe 3$d$ and O 2$p$ orbitals, with the O 2$p$ electrons being predominant. The calculated electron and hole effective masses are $1.6m_0$ and $2.2m_0$, implying sluggish mobility of carriers and poor conductivity. Hematite stands out as a promising photoanode material due to the desired properties include: 1) suitable band gap (2.0-2.2 eV), 2) high chemical stability in alkaline environments, 3) inherent non-toxicity, and 4) earth-abundance and low-cost. Despite its many advantageous features, the practical PEC performance of the Fe$_2$O$_3$ photoanode is much lower than theoretical expectations. This is primarily due to its inferior electrical conductivity ($10^{-12}$-$10^{-13}$ $\Omega^{-1}$ cm$^{-1}$), limited hole diffusion length (around 2-4 nm), constrained charge carrier lifetime (<0.4 ns), poor hole mobility ($10^{-7}$-$10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$), and slow water oxidation kinetics.
Furthermore, the more positive CBM of hematite relative to RHE potential leads to a high onset potential for solar water splitting (Figure 37).

Numerous studies and review articles have delved into hematite modification strategies, including morphology control, doping, heterojunction formation, surface passivation, cocatalysts modification, etc., aiming to enhance charge transfer efficiency. Through various modification techniques, there has been a marked reduction in onset potential drop and an increase in saturated photocurrent (Figure 40). Notably, integrating multiple strategies has achieved a stable photocurrent density of approximately 6 mA cm\(^{-2}\) at 1.23 V vs. RHE under one-sun illumination. To conclude, despite significant advancements, there remains a considerable journey ahead to fully harness the potential of \(\alpha\)-Fe\(_2\)O\(_3\) to achieve the theoretical photocurrent value of over 10 mA cm\(^{-2}\) with a low onset potential near its Fermi level (~0.4 V vs. RHE).

**Figure 40.** Summary of (a) photocurrent density and (b) onset potential of selected \(\alpha\)-Fe\(_2\)O\(_3\) photoanodes. Adapted with permission from reference 369, Copyright 2018, Wiley-VCH.
Stabilizing high efficiency/low durability PV materials. Semiconductors used in photovoltaic applications generally refer to materials like silicon, GaAs, GaAlAs, InP, CdS, CdTe, CuInS₂, and CuInGaSe₂. These compounds are characterized by high carrier mobility and long diffusion lengths, making them particularly efficient in converting sunlight into electrical energy in PV devices. Utilizing the exceptional properties of PV-grade materials, high solar water splitting efficiencies of over 10% have been achieved in PV-EC, PEC, and hybrid cells. However, PV materials exhibit limited resistance to photo-corrosion, especially in alkaline/acidic aqueous solutions, necessitating specialized surface protection and encapsulation techniques to ensure long-term stability during water splitting operations. Besides, the broad application of most PV materials is restricted due to relatively high production costs and energy-intensive manufacturing processes. Many review articles have summarized the comprehensive understanding and protection strategies of conventional PV material-based photoanodes.

Figure 41. Schematic diagrams of (a) Z-scheme PEC, (b) PV-EC, and (c) PVM-PEC systems. Scheme diagrams of temperature effects on LSV curves and operation points of (d) Z-scheme PEC, (e) PV-EC, and (f) PVM-PEC devices. HT = high temperature; LT = low temperature.

One of the most advantages of PV materials-based photoelectrochemical cells (PVM-PEC) over the PV-EC configuration is the superior thermal management. In the PEC system, when heated by incident light after specific modification, the simultaneously enhanced catalytic kinetics for each photoelectrode lead to an increased operation current (Figure 41a and 41d), which can indirectly expand the spectral utilization range. However, in PV-EC systems, when solar panels are inevitably heated under illumination, the
decrease in FF and $V_{oc}$ directly results in a reduction of operational current (Figure 41b and 41e), and the required cooling equipment inevitably increases the total costs. The PVM-PEC configuration overcomes the disadvantage of panel heating in the PV-EC system. The enhanced catalytic performance at high temperatures compensates for performance loss in FF and $V_{oc}$, which delivers an increased photocurrent under higher bias (Figures 41c and 41f). Photothermal heat can be efficiently transferred to the catalyst layer through a reasonable structural design, avoiding performance and stability losses caused by heat accumulation while also accelerating the reaction kinetics. The advanced PV materials used in PVM-PEC deliver significantly better performance than those oxides used in traditional PEC, making PVM-PEC highly competitive with traditional PEC. Moreover, short charge migration distance in integrated PVM-PEC configuration facilitates the scalability without the problem of linearly increasing series resistance as the PV area increases, reducing the complexity of the system, which outperforms the PV-EC system.

1.4.3 Lead halide perovskite-based photoanodes

Since the first report in 2009 highlighting the photovoltaic potential of organic-inorganic lead halide perovskites, various metal halide perovskite materials (MHP), notable for their superior optical and electronic properties, have been identified as compelling alternatives to traditional metal-oxide/nitride/chalcogenide semiconductor-based photocatalysis systems. Figure 42a illustrates the components of a perovskite structure where 'A' is a monovalent cation, 'B' is a bivalent cation, and 'X' is a monovalent anion. In most widely-used MHP solar cells, 'A' corresponds to CH$_3$NH$_3^+$ (MA), CH(NH$_2$)$_2^+$ (FA), Cs$, etc.; 'B' includes Pb$^{2+}$, Sn$^{2+}$, etc.; and 'X' can be Cl$^-$, Br$^-$, or I$^-$. MHPs possess exceptional optoelectronic characteristics, including extended carrier lifetimes, high trap densities tolerance, long electron/hole diffusion length, high optical absorption, and a modifiable band gap that supports a wide photon absorption from ultraviolet (UV) to near-infrared (IR) wavelengths. The progress of MHP-based PVs has been remarkable, with single junction devices reaching a PCE of 26.1% to date. MHPs stand out as high-efficiency semiconductors with cost-effective synthesis methods and impressive power conversion efficiency, paving the way for advanced perovskite-driven solar-to-fuel systems.

As a novel type of PVM-PEC photoanode, MHP-based photoanodes share architectural similarities with associated PV devices. Typically, an MHP-based photoelectrode is structured with a perovskite layer for effective light absorption, accompanied by an electron transport layer (ETL), a hole transport layer (HTL), surface passivation layer(s), and catalytic layer(s) to
enhance the HER/OER reactions (Figure 42b). When exposed to light, the MHP layer produces excitons upon absorbing photons. These generated electrons and holes then migrate to the ETL and HTL, respectively. In photoanodes with an n-i-p configuration, the excited electrons move towards the transparent conducting oxide (TCO) current collector through the ETL, while the holes are channeled by the HTL, passing through the surface passivation layer to participate in the OER at the electrode/electrolyte interface. The efficiency and stability of the MHP-based PEC cell mainly depend on the quality of the perovskite layer, the optimization of carrier transporting layers, the encapsulation techniques, and the performance of the catalytic layer.

**Figure 42.** (a) Schematic diagram of ABX$_3$ type perovskite. (b) Schematic illustration of perovskite-based photoanode for oxygen evolution. (c) Band positions of MHPs in the pH 13.6 aqueous electrolyte compared with the energy potential for water splitting reaction. Red = valence band edge; blue = conduction band edge. (d) Comparison of the LSV curves between the FAPbBr$_3$ photoanode and other perovskite photoanodes made from a single junction absorber layer including CsPbBr$_3$, FAMAPbI$_3$, and FA$_{0.83}$Cs$_{0.17}$Pb(I$_{0.8}$Br$_{0.2})_3$. The LSV data was extracted from corresponding literature.

**Composition.** Lead halide perovskites with iodide components possess a notable theoretical saturation current due to their narrow band gap (Figure 42c). However, generating the requisite photoelectric voltage for water oxidation remains challenging for a single cell. Therefore, when employed as
a single junction photoanode, they often exhibit an onset potential exceeding 0.5 V vs. RHE (Figure 4d). On the other hand, chloride perovskites are hindered by their broad band gap, resulting in significantly reduced visible light absorption. In contrast, bromide perovskites, given their ideal energy structure alignments, are preferred choices for developing photoanodes with a reduced onset potential. Bromide perovskites exhibit band gaps between 2.2-2.4 eV and the theoretical Shockley-Queisser efficiency limit of approximately 15%. Remarkably, bromide perovskites with single A-site cations, such as MA, FA, and cesium, demonstrate enhanced stability in the photoactive phase compared to iodide counterparts. Among these, CsPbBr$_3$ possesses the widest band gap of 2.4 eV, leading to the smallest theoretical saturation current. Additionally, its inorganic composition often requires high-temperature processing over 300 °C, posing challenges in controlling the phase purity. Meanwhile, MAPbBr$_3$ components lack thermal resilience, making them unsuitable for long-term high-temperature operations. Indeed, when subjected to heat and moisture, MAPbX$_3$ can decompose into gaseous methylamine and hydrogen halide, resulting in reduced optical extinction coefficient and severe charge carrier recombination. In contrast, the ionic radius of FA$^+$ is larger than that of MA$^+$, giving FAPbBr$_3$ a greater lattice constant than MAPbBr$_3$, leading to enhanced structural and thermal stability. Besides a stable phase and facile fabrication conditions, FAPbBr$_3$ also demonstrates an outstanding carrier diffusion length of 19 µm, ranking among the highest in halide perovskite materials. Therefore, after weighing the factors of fabrication complexity, energy band structure, and material stability, FAPbBr$_3$ emerges as the prime candidate for producing single-junction photoanodes with minimized onset potential and suitable saturation current.

**Preparation methods of the perovskite layer.** The method used to prepare the MHP light-absorbing layer is pivotal for the performance of PV and PEC devices. Ideally, a perovskite film should be crystalline, dense, and smooth to enhance the generation and separation of photogenerated carriers. In contrast, a rough film with evident pores reduces photovoltage and current, creates a recombination pathway by directly connecting the ETL and HTL, and introduces trap states that serve as carrier recombination centers. The quality parameters of the MHP-based film depend on the perovskite synthesis process. Presently, methods to prepare lead halide perovskite composite films include one-step spin coating, two-step procedures like stepwise liquid immersion and spin coating, co-evaporation, stepwise gas-assisted deposition, etc.
Electron/hole transport layer. Transparent metal oxide semiconductors, such as TiO$_2$, ZnO, and SnO$_2$, are the most used ETLs in MHP-based photoelectrode. Their primary function is to efficiently transfer photogenerated electrons from the perovskite layer while blocking holes (Figure 43). To enhance the performance of the MHP-based photoelectrode, it is crucial to design and optimize the ETL by considering factors like band alignment, diffusion length, and electron mobility. Conversely, the HTL collects and transports the photogenerated holes from the perovskite layer, inhibiting electron-hole recombination. Various materials, both organic and inorganic, have been investigated as HTLs. Notable examples include spiro-OMeTAD (2,2,7,7-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene), PEDOT:PSS (poly (3,4-ethylene dioxythiophene) polystyrene sulfonate) and PTAA (poly bis(4-phenyl)(2,4,6-trimethylphenyl)amine). Of these, spiro-OMeTAD with Li dopants stands out for its performance. However, concerns arise due to its high cost and the potential of salt-dopant diffusion into the perovskite layer, leading to perovskite decomposition and performance decay. The topic of preparation methods of MHP film and selection of HTL/ETL is strongly connected to PV technologies, which extends beyond the scope of the thesis and, as such, will not be detailed further in this context.

![Figure 43. Energy bands of the materials in MHP-based PEC cells.](image)

Surface encapsulation. MHPs exhibit high sensitivity to environmental factors and readily decompose into their binary components when exposed to polar solvents, moisture, oxygen, irradiation, or heat. Therefore, PEC systems utilizing MHPs necessitate effective surface encapsulation to protect the perovskite layers from chemical reactions, moisture penetration, and structural changes. These materials should possess good electrical and
thermal conductivity coupled with effective water resistance. Simultaneously, their exterior surface should remain stable under harsh OER conditions and accommodate a substantial quantity of catalysts. Various encapsulation techniques, including Field's metal,\textsuperscript{392} metal foil,\textsuperscript{393} carbon,\textsuperscript{394} and graphite\textsuperscript{383},\textsuperscript{385} layers, have been developed for MHP-based photoelectrodes. Nonetheless, the achieved stability remains restricted, often lasting less than 100 hours, particularly for photoanodes.\textsuperscript{395} In contrast, the standalone PV devices usually exhibit stability exceeding 100 hours. In some studies, the degradation of perovskite photoanode devices is clearly attributed to water penetration, underscoring the importance of efficient encapsulation techniques in advancing perovskite photoanodes.\textsuperscript{383, 386, 396}

**WOC layer.** To date, there are only limited studies on MHP-based photoanodes compared to typical oxide-based devices. Most employed catalysts are primarily nickel-based, including metallic Ni,\textsuperscript{385} NiFe alloy,\textsuperscript{384} NiFe (oxy)hydroxide,\textsuperscript{397} and NiS.\textsuperscript{398} Additionally, Poli and co-workers successfully demonstrated the use of immobilized molecular Ir WOC with a CsPbBr\textsubscript{3} photoanode.\textsuperscript{383} Using a more efficient WOC can reduce the overpotential for water oxidation, reducing the onset potential. Meanwhile, rapid charge consumption prevents charge accumulation within the perovskite layer, averting potential radiative recombination and subsequent perovskite structure degradation. Currently, the stability of the catalysts is not considered as the primary constraint on the durability of perovskite photoanode devices. Many material WOCs, especially those (hydro)oxides under alkaline conditions, can operate stably for over 1000 hours.\textsuperscript{399, 400} As advancements in WOCs continue, the variety of catalyst-modified perovskite photoanodes is expected to expand significantly.

**Perspective.** MHPs exhibit characteristics that are highly advantageous for photoelectrochemical cells. Their adjustable band gaps ensure optimal light capture, while the facile charge separation promotes effective solar-to-chemical energy transformation. Efficient photocarrier utilization in MHPs results in a high photocurrent density and a reduced onset potential for PEC devices, significantly surpassing traditional photoanodes. Additionally, most MHP materials can be produced using straightforward, scalable, and cost-effective solution-based synthesis methods, offering advantages over traditional III-V semiconductor-based devices. Despite their remarkable features, long-term stability is the primary challenge in developing MHP-based PEC cells. MHPs are notably sensitive to conditions, such as moisture, temperatures, and UV radiation. When MHPs are used directly as light absorbers in PEC cells under aqueous solutions, the perovskite layer tends to degrade rapidly, leading to performance loss and lead poisoning. Even upon
incorporation of suitable encapsulation layers, the lifetime of MHP-based photoelectrodes, particularly photoanodes operating under oxidative potentials, remains insufficient. Figure 44 presents the stability data of various reported photoanodes with different encapsulation strategies. Regrettably, all devices exhibit a pronounced current decay under operational potential. Several factors might contribute to this, including photo/thermal degradation of the perovskite layer, catalyst layer degradation or detachment, perovskite ion migration under bias, water penetration, etc. Therefore, focus should be placed on stabilizing and protecting MHPs through rational structural and compositional design.

Enhancing the stability of perovskite photoanodes can be categorized into three dimensions: intrinsic stability of the perovskite cell, intrinsic stability of the catalyst, and encapsulation robustness. The stability of the perovskite cell component can be enhanced through various established methods, including the use of additives, solvent optimization, interface design, advancements in charge transport materials. A comprehensive overview has been summarized in relevant review articles. There is a significant lack of stable encapsulation techniques that are resistant to harsh aqueous solutions, highlighting a critical area for future development. Enhancing device stability can be achieved through optimized operating conditions. The n-i-p structured solar cells often exhibit reversible losses, where efficiency improvements are noted upon re-measurement after a period of darkness (Figure 45a). Such a "dark recovery" approach has proven effective in enhancing the stability of perovskite devices, as evident in PV device applications (Figure 45b). Therefore, applying a light-dark cycling strategy could be beneficial...
in extending the lifetime of perovskite PEC devices. Moreover, optimizing device stability can be accomplished by designing devices for neutral electrolytes, lowering operational bias, filtering ultraviolet light, and employing potential strategies inspired by other PEC systems.

Figure 45. (a) Aging perovskite devices show significant efficiency recovery after resting in the dark. Adapted with permission from reference 404, Copyright 2018, Elsevier. (b) The effect of light cycling on aging. Adapted with permission from reference 407, Copyright 2020, Springer Nature.

1.5 The aim of this thesis

The key scientific challenge in artificial photosynthesis is efficient water oxidation catalysis and effective light harnessing. In pursuit of developing advanced (photo)electrochemical water oxidation systems and unraveling the structure-activity relationship, this thesis aims to:

1) Immobilize host-guest cobalt WOC onto the surface of conductive/semiconductor electrodes for efficient (photo)electrochemical-driven water oxidation and investigate the charge transfer kinetics behaviors in this WOC-modified photoanode.

2) Fabricate efficient heterogeneous WOC with well-defined molecular cobalt sites and investigate the water oxidation kinetics for discerning the crucial role of electrolyte pH in regulating the O-O bond formation mechanism.

2. Methodology

2.1 Material characterizations

**Powder X-ray diffraction (XRD).** The crystal structures were characterized through powder XRD analysis. XRD studies were performed on two types of instruments: i) Bruker D8 Advance Power X-Ray Diffractometer (Cu-Kα radiation, λ = 1.5418 Å); ii) Siemens D5000 0-2θ goniometer with Cu Kα (λ = 1.5418 Å) radiation and a 0.4° Soller slit collimator (Bruker AXS).

**X-ray photoelectron spectroscopy (XPS).** The surface chemical state of the samples was investigated by XPS using two types of instruments: i) a PHI Quantera II from Physical Electronics and ii) a Thermo Scientific ESCALAB Xi+, both with monochromatized Al Kα radiation sources (1486.6 eV). The binding energy calibration was performed using the C 1s core level of adventitious carbon. The ultraviolet photoelectron spectroscopy (UPS) spectra were acquired using a Thermo Scientific ESCALAB Xi+ with excitation provided by the He I emission line (21.2 eV).

**X-ray absorption spectroscopy (XAS).** The X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements were carried out at beamline 07A1 of Taiwan Light Source (TLS) of the National Synchrotron Radiation Research Center (NSRRC). This beamline adopted fixed-exit double crystal Si(111) monochromator to ranging the X-ray energy within 5-23 keV. The end-station equipped ionization chambers and a Lytle detector for transmission and fluorescence mode X-ray absorption spectroscopy. The data were collected in fluorescence mode using a Lytle detector, while the corresponding reference sample was collected in transmission mode. The powder samples were ground and uniformly smeared on special adhesive tape. The EXAFS raw data were performed according to the standard procedures with ATHENA software packages. The quantitative curve-fittings were carried out in the R-space (1.0-3.0 Å) with a Fourier transform k-space range of 2.5-12 Å⁻¹ by using the module ARTEMIS of IFEFFIT. The wavelet transform (WT) for EXAFS was calculated by HAMA FORTRAN software.

**Fourier transform infrared (FT-IR).** The infrared spectra of the fabricated samples were characterized by two types of instruments: i) a Bruker Vertex 70v spectrometer by the sampling methodology of attenuated total reflectance (ATR) with background correction; ii) Thermo Fisher Nicolet 6700 Flex spectrometer using ATR mode.
**Inductively coupled plasma-optical emission spectroscopy (ICP-OES).** The concentration of metal was measured using ICP-OES with a Thermo Scientific iCAP 6000 series instrument. Metal standard solutions were measured prior to the samples to calibrate and obtain the standard curve. Co concentrations were determined using four different wavelengths: 231.1 nm, 235.3 nm, 237.8 nm, and 238.8 nm. The average concentrations obtained at different wavelengths were taken for data evaluation.

**Atomic force microscope (AFM).** Atomic Force Microscopy (AFM) analyses were conducted on a Cypher ES system, operating in dynamic mode under ambient air conditions at room temperature. A commercial Oxford probe (HQ-150-Au) with a nominal force constant of 8 N/m was employed. Silicon dioxide on silicon (SiO$_2$/Si) wafer served as the substrate for the AFM experiments, and the acquired images were analyzed using Gwyddion software.

**Scanning tunneling microscopy (STM).** The STM experiments were performed in a qPlus-equipped commercial Omicron LT-STM (Omcron LT-STM QPlus pre4) at 4.2 K. The sample was deposited on the pre-cleaned Au(111) substrate by *in-situ* thermal evaporation under ultrahigh vacuum conditions. The STM image was obtained at a sample bias of 0.2 V and a tunneling current of 50 pA.

**Scanning electron microscope (SEM).** The morphology and composition of the fabricated samples were characterized by two types of SEM instruments: i) ZeissLEO1530/1550 SEM with an energy-dispersive X-ray spectroscopy (EDS) detector (Oxford AZtec EDS system); ii) a Hitachi field-emission SEM (Regulus 8230) with an EDS detector (Oxford Ultim EXTREME).

**Transmission electron microscopy (TEM).** High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images, along with EDS mapping images, were acquired using an aberration-corrected JEOL JEM ARM-200F microscope and a FEI Talos F200X microscope.

**Nuclear magnetic resonance (NMR).** High-resolution solid-state NMR spectra were acquired using a Bruker Avance III spectrometer, operating at a Larmor frequency of 125.7 MHz and equipped with a 4 mm broadband cross-polarization magic angle spinning (CP-MAS) probe. Alanine served as an external reference, with a chemical shift of 178 ppm. The sample spinning rate for MAS was set at 8 kHz. Cross-polarization was implemented with a contact pulse duration of 1 ms and a recycle delay of 5 s. A total of 2740 transients were required to achieve an optimal signal-to-noise ratio.
Nitrogen sorption isotherms. Nitrogen sorption isotherms were acquired at 77 K using a Micromeritics 3Flex adsorption analyzer. Prior to analysis, samples were degassed under vacuum conditions at 150 °C for 12 hours. Specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method, while the porosity of the samples was assessed through non-local density functional theory (NLDFT) models utilizing SAIEUS software.

Faraday efficiency. Faraday efficiency measurements were conducted using two different methods: i) an Omega PXM409 pressure transducer in conjunction with a laboratory-made H-cell; ii) gas chromatography (Techcomp GC 7890T, Ar carrier gas, thermo conductivity detector).

Mass spectrum. The mass spectrum of complex sample was obtained using electrospray ionization-mass spectrometry (Q-TOF Micro, Micromass).

2.2 Electrochemical measurements

All electrochemical characterizations were conducted at 25°C, unless otherwise specified, with temperature regulation via a thermostatic water bath. OER was examined using a standard three-electrode cell connected to a CHI 660c/760e electrochemical workstation. The as-prepared materials served as the working electrode, platinum mesh acted as the counter electrode, and either Hg/HgO in 1.0 M KOH or Ag/AgCl in saturated KCl was employed as the reference electrode. The cell was fabricated from PTFE to mitigate potential iron contamination. Measured potentials were normalized to the reversible hydrogen electrode using the equation: Potential = E\text{ref} + E\text{(ref vs. RHE)}; E\text{(ref vs. RHE)} is the potential difference between the reference electrode and RHE at 25°C for the electrolytes, which is corrected by a commercialized RHE (HydroFlex of Gaskatel). LSV curves were recorded with 95% iR-correction. The correction was done manually through the equation: E\text{corr} = E\text{meas} – iR_u, where E\text{corr} is iR-corrected potential, E\text{meas} is an experimentally measured potential, and R_u is the equivalent series resistance extracted from the Nyquist plots. The calculation of Tafel slopes was conducted through curve fitting of the polarization data, utilizing the subsequent equation: $\eta = b \times \log(j) + a$, where $\eta$ is overpotential (mV), $j$ is the current density (mA cm$^{-2}$), and $b$ is the Tafel slope. Chronopotentiometry was recorded under the same experimental setup without iR drop.

TOF calculation. The TOF of the catalyst was calculated by Equation 19.

$$\text{TOF} = \frac{jA}{4FA} \quad (19)$$
Where \( j \) is the OER current density, which was obtained from LSV under a low scan rate; \( A \) is the surface area of the electrode; \( F \) is the Faraday constant (96485 C mol\(^{-1}\)), and \( \Gamma \) is the number of metal centers obtained from i) the linear relationship between loading and the redox peak current \( i_p \) or ii) total metal content from ICP-OES tests.

Specifically, Equation 20 establishes a linear relationship between the peak current \( i_p \) (the redox peak of \( \text{M}^{n+/(n+1)+} \)) and the loading of redox-active metal sites \( (\Gamma, \text{mol cm}^{-2}) \).

\[
    i_p = \frac{n^2F^2\nu A\Gamma}{4RT} \tag{20}
\]

Where \( n \) is the number of electrons (for \( \text{M}^{n+/(n+1)+} \), \( n = 1 \)), \( \nu \) is scan rate (V s\(^{-1}\)), \( A \) is surface area (cm\(^2\)), \( F \) is the Faraday constant, \( R \) is the ideal gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)), \( T \) is the temperature (298 K).\(^{412}\)

Then the loading of redox-active \( \text{M}^{n+} \) sites could be estimated based on the linear relationship between the peak current of the redox wave and the scan rates (Equation 21).

\[
    \text{Slope} = \frac{n^2F^2A\Gamma}{4RT} \tag{21}
\]

**Kinetic isotope effects experiments.** KIEs were assessed using electrochemical methods. The LSV or cyclic voltammetry (CV) was recorded with a scan rate of 5 mV s\(^{-1}\) and \( iR \) compensated (95%). In alkaline conditions, experiments were carried out in a 1.0 M NaOH aqueous solutions and 1.0 M NaOD in D\(_2\)O solutions. In near-neutral conditions, anhydrous sodium tetraborate solutions in H\(_2\)O ([Bi]=0.1 M) and D\(_2\)O ([Bi]=0.1 M) were employed. The pH of the H\(_2\)O and D\(_2\)O borate buffers was measured to be 9.1 and 9.2, respectively. The current densities at a specified overpotential, \( \eta \), were denoted as \( j_{\text{H}_2\text{O}} \) and \( j_{\text{D}_2\text{O}} \). KIEs\(_{(\text{H}/\text{D})}\) were then calculated based on a specific equation.

\[
    \text{KIEs}_{\text{H}/\text{D}} = \left[ \frac{j_{\text{H}_2\text{O}}}{j_{\text{D}_2\text{O}}} \right]_\eta \tag{22}
\]

The overpotential was corrected according to our previously reported method.\(^{214}\)

**pH-dependence characterizations.** LSV or CV scans were conducted with 95% \( iR \) compensation across varying concentrations of sodium hydroxide.
solutions, specifically 0.0625 M, 0.125 M, 0.25 M, 0.5 M, and 1.0 M. The pH values for these NaOH solutions were measured using a specialized pH-electrode, pHydrunio, designed to accurately measure hydrogen ion activity in highly concentrated alkaline solutions. The recorded pH values for 0.0625 M, 0.125 M, 0.25 M, 0.5 M, and 1.0 M NaOH solutions were 12.49, 12.81, 13.11, 13.37, and 13.61, respectively. For experiments in near-neutral conditions using NaBi-buffered solutions, pH was adjusted using 0.5 M H$_3$BO$_3$ and 0.5 M NaOH solutions and measured using a conventional pH meter. The reaction order with respect to OH$^-\$ is then calculated based on a specific formula:

$$\rho_{[\text{OH}^-]} = \frac{\partial \log j}{\partial (\text{pH})} = \frac{\partial \log j}{\partial \text{pH}} \tag{23}$$

Where $j$ is the current density (mA cm$^{-2}$) at a certain overpotential $\eta$, [OH$^-$] is the concentration of hydroxide in electrolytes (mol L$^{-1}$).

**Anion dependence electrochemistry.** In water oxidation pathway follows a concerted solution APT with O-atom of a water molecule transfer to the M=O coupled with a proton transfer to the base acceptor(s) in solution (Equation 24), the current density is linearly related to the concentration of anions, as outlined in Equation 25.

$$\frac{jA}{4F \Gamma} \eta = k^{H_2O} + k^{B}[B] \tag{25}$$

Where $A$ is the surface area (cm$^2$) of the electrode, $F$ is the Faraday constant, $\Gamma$ is the number of electroactive species (mol cm$^{-2}$), $j$ is the current density (mA cm$^{-2}$), and [B] is the concentration of additional anions (mol L$^{-1}$). Thus, the reaction order for additional anions (external bases) in solutions, denoted as $\rho[B]$, can be determined using the following equation:

$$\rho_{[B]} = \frac{\partial \log j}{\partial \log [B]} \eta \tag{26}$$

In the measurements, the total concentration of buffer components was increased while pH was held constant. Borate buffers at near neutral
conditions with different concentrations were formulated by solubilizing boric acid in water, with pH adjusted using 10 M NaOH. For borate solutions at strong basic conditions with different concentrations, sodium tetraborate was dissolved in water, and pH was also adjusted with 10 M NaOH. The phosphate buffers at around pH 12.6 with different concentrations were prepared by dissolving tri-potassium phosphate in water, and the pH was adjusted by 10 M KOH. Then $\rho_{\text{borate}}$ and $\rho_{\text{phosphate}}$ were calculated according to Equation 26.

**Cation dependence electrochemistry.** The presence of ions in water seriously affects the H-bond network. K$^+$ is more efficient in breaking the H-bond network than Na$^+$ and Li$^+$.\(^{413}\) Aside from modifying the hydrogen bonding network, the cations also possess different solvation strengths (Li$^+ >$ Na$^+ >$ K$^+$). The kinetics associated with the nucleophilic attack of water on oxidized electrophilic species is decreased when increasing the solvation strength (Equation 27).\(^{414}\)

$$M=O + H_2O + OH^- \rightarrow M-O\overset{\delta^-}{\cdots}O\overset{\delta^-}{\cdots}H + OH^- \rightarrow M-OOH + H_2O \quad (27)$$

For experiments under strongly basic conditions, LSV or CV curves were obtained with 95% $iR$ compensation in 1.0 M solutions of sodium, potassium, and lithium hydroxide. The pH levels for these 1.0 M NaOH, KOH, and LiOH solutions were determined using a pHdrunio pH-electrode, yielding measured pH values of 13.61, 13.63, and 13.34, respectively. In near-neutral conditions, LSV or CV curves were acquired with 95% $iR$ compensation in 0.5 M borate buffer solutions of sodium, potassium, and lithium. These 0.5 M NaBi, KBi, and LiBi solutions had pH values of 9.28, 9.43, and 9.10, respectively. All measured potentials were converted to the RHE scale for comparative analysis of current densities.

**Temperature dependence electrochemistry.** Electrocatalytic experiments were conducted under regulated temperature conditions in both alkaline (1.0 M NaOH) and near-neutral (0.5 M NaBi) environments to determine the activation energy of the RDS for specific catalysts. In such activation energy measurement, the catalytic rate, i.e., current densities, should be contrasted at the same overpotential. As deduced in paper II, the overpotential at a specific temperature in 1.0 M NaOH electrolyte can be corrected by Equation 28.
The overpotential at a specific temperature in 0.5 M NaBi electrolyte can be corrected by Equation 29.

\[
\eta_{\text{H}_2\text{O}}^{\text{Hg/HgO}} = E_{\text{Ag/AgCl}}^{\text{read}} + \frac{RT}{F \times \log_{10}e} \log \left[ \frac{k_w}{0.668} \right] + [0.098 - 0.0011 \times (T - 298.15)] - (1.48 - 0.000843 \times T) \tag{28}
\]

Where \( E_{\text{Ag/AgCl}}^{\text{read}} \) is the potential read by the reference electrode in the electrolyte at the specific temperature, \( k_w \) is the ionic product of water that can be read from Figure 46.

\[ k = A e^{-W/RT} \tag{30} \]

For catalytic conditions, the rate constant \( k \) for electrocatalytic reactions shows a dependency on the applied overpotential, as described by Equation 31.

\[ k = k_0 e^{(1-\alpha)F\eta/RT} \tag{31} \]

Where \( k_0 \) is the standard rate constant, \( F \) is the Faraday constant, \( \alpha \) is the transfer coefficient. \( E_a \) was defined as the activation energy at the equilibrium potential (zero overpotential), thus:
\[ k_0 = Ae^{-E_a/RT} \quad (32) \]

Then the relationship between \( W \) and \( \eta \) can be deduced by combining Equations 30, 31, and 32:

\[ W = E_a - (1 - \alpha)F\eta \quad (33) \]

Therefore, \( W \) changes linearly with \( \eta \), and the y-axis intercept of the line is the activation energy at the equilibrium conditions (\( E_a \)). When the mass transport effects on the OER are assumed to be negligible, the Arrhenius equation can be written in the form below:

\[ i_k = Ae^{-W/RT} \quad (34) \]

Where \( i_k \) is kinetic current. In summary, the value of \( W \) can be calculated through linear fitting, as outlined in Equation 34. Subsequently, the activation energy \( E_a \) can be extracted from the linear correlation between \( W \) and \( \eta \), as described in Equation 33.

2.3 Photoelectrochemical measurements

All photoelectrochemical measurements were performed at ambient temperature utilizing CHI 660e/760e electrochemical workstation. The photoanodes under examination were employed as the working electrode in a three-electrode setup, accompanied by a Pt mesh counter electrode and Hg/HgO (1.0 M KOH) or Ag/AgCl (saturated KCl) reference electrodes. All potential readings were calibrated to correspond to the RHE scale using a commercially available RHE reference (HydroFlex of Gaskatel) at 25°C. The simulated solar illumination was obtained by two types of solar simulators: i) 300 W Xenon arc lamp (EXCELITAS, PE300BFA) equipped with an AM 1.5G filter; ii) 100 W Xenon arc lamp (NEWPORT LCS-100, type 94011A-ES) with an AM 1.5G filter. The incident light power intensity was calibrated to 100 mW cm\(^{-2}\) by a photometer. \( J-V \) curves were obtained by LSV without \( iR \)-correction. The long-term electrolysis was performed under a constant potential using the same experimental setup.

**Intensity Modulated Photocurrent Spectroscopy.** IMPS spectra were recorded by a Zahner IMPS electrochemical workstation. Intensity-modulated light was provided by a white light-emitting diode with a light intensity of 100 mW cm\(^{-2}\) that allowed the superimposition of sinusoidal modulation (\(~10\%) on a DC illumination level. The modulation amplitude of the lamp voltage was 2 mV. The IMPS data was recorded at different applied potentials over the 1 kHz-50 MHz frequency range. The rate constants for
interfacial charge transfer ($k_{\text{trans}}$) and charge recombination ($k_{\text{rec}}$) were extracted from IMPS plots featuring two semicircles in both the first and fourth quadrants. The points where these semicircles intersect with the real axis (x-axis) at low and high frequencies denote $I_1$ and $I_2$, respectively. The frequency at the peak of the upper semicircle, denoted as $f_{\text{max}}$, indicates relaxation in the hole concentration. The rate constants $k_{\text{trans}}$ and $k_{\text{rec}}$ can thus be calculated by the following equations:

$$2\pi f_{\text{max}} = k_{\text{trans}} + k_{\text{rec}} \quad (35)$$

$$I_1 = I_2 \times \frac{k_{\text{trans}}}{k_{\text{trans}} + k_{\text{rec}}} \quad (36)$$

The $I_1/I_2$ ratio signifies the portion of holes reaching the surface that successfully get injected into the electrolyte, commonly referred to as the effective surface charge transfer efficiency ($\eta_{\text{surface}}$).

$$\eta_{\text{surface}} = \frac{k_{\text{trans}}}{k_{\text{trans}} + k_{\text{rec}}} \quad (37)$$

**Applied bias photon-to-current efficiency (ABPE).** The ABPE was calculated from the $J-V$ curves under illumination (in a three-electrode system) using the following equation:

$$\text{ABPE(\%) = } \frac{(1.23 - V_{\text{RHE}}) \times (j_{\text{light}} - j_{\text{dark}})}{P_{\text{light}}} \times 100\% \quad (38)$$

Where $V_{\text{RHE}}$ indicated the applied potential under the RHE scale, $P_{\text{light}}$ was the light intensity of incident light (AM 1.5G), $j_{\text{light}}$ and $j_{\text{dark}}$ were photocurrents and dark current, respectively.

**Incident photon-to-current efficiency (IPCE).** The IPCE values of photoanodes were calculated using the following equation:

$$\text{IPCE(\%) = } \frac{1240 \times (j_{\text{light}} - j_{\text{dark}})}{\lambda \times P_{\lambda}} \times 100\% \quad (39)$$

The monochromatic light was generated using a monochromator. The light intensity ($P_{\lambda}$) at each wavelength ($\lambda$) was determined by a photometer; $j_{\text{light}}$ and $j_{\text{dark}}$ were measured photocurrent and dark current, respectively.

**Onset potential and photovoltage.** The $E_{\text{onset}}$ of the photoanode was determined by the point where the $J-V$ curve intersects the x-axis. The related $V_{\text{ph}}$ was then computed using the following equation:
\[ V_{ph} = 1.23 - E_{onset} \, (25^\circ C) \quad (40) \]

**Surface charge separation efficiency.** The surface charge separation efficiency (\(\eta_{\text{surface}}\)) was calculated using the following equation:

\[ \eta_{\text{surface}} = \frac{j_{\text{water}}}{j_{\text{sulfite}}} \quad (41) \]

Where \(j_{\text{water}}\) is the current density of water oxidation at a certain applied potential, \(j_{\text{sulfite}}\) is the current density of hole scavenger (sodium sulfite) oxidation at the same applied potential.

### 2.4 Notes for pH dependency of OER activity

The RDS of a specific water oxidation catalysis system may be classified into three types: ET-controlled RDS, PT-controlled RDS, and CPET-controlled RDS. The reaction order of OER activity with pH shows how OER kinetics depend on proton activity. When excluding the change in the number of catalytic sites under different pH, measuring the pH dependence of the OER activity could provide insights into the proton-electron transfer features of RDS in the specific reaction pathways. Theoretically, a zeroth-order reaction would imply no dependence, which is usually observed in catalysis that was controlled by a CPET step; when a sequential PT or ET transfer step is the RDS (proton transfer and electron transfer steps are decoupled), an OER catalyst could exhibit pH-dependent OER activity. Fractional reaction orders may also be expected when the mechanism consists of complex chain/side reactions.\(^{416-419}\)

#### 2.4.1 Explanation of pH dependence

The pH-dependent OER activity (i.e., reaction order of pH) is quantitatively analyzed by rational quantitative CV analysis as established below.\(^{420}\) To simplify the analysis, the pre-RDS reaction \(M^{n+} - e^- \rightarrow M^{(n+1)+}\) was assumed to be an irreversible one-step, one-electron reaction, and \(M^{(n+1)+}\) will be consumed for OER by another irreversible reaction \(M^{(n+1)+} - e^- \rightarrow M^{(n+2)+}\) that was assigned as the RDS for the whole reaction. Then, the expected current-potential behavior of the pre-RDS reaction is given by the following equation (see **Paper II** for detailed derivation):

\[
i_{\text{pre}} = \left( \frac{F^2}{RT} \right) \left( 1 - \alpha \right) e^\Gamma \times \exp \left[ \left( \alpha \frac{F}{RT} \right) (E - E_p) \right] \\
\times \exp \left\{ -\exp \left[ \left( \alpha \frac{F}{RT} \right) (E - E_p) \right] \right\} \quad (42)
\]
The OER current-potential behavior based on RDS reaction in the foot of wave area could be written as the equation below:

$$i_{OER} = 4k_{ap}[a]F\Gamma \frac{1 - \exp \left\{ -\exp \left[ \frac{(1 - \alpha)F}{RT} (E - E_p) \right] \right\}}{1 + \exp \left[ (E - E_r)F/RT \right]} \tag{43}$$

Where $F$ is the Faradaic constant, $k_{ap}$ is the apparent rate constant, $v$ is scan rates, $[a]$ is the activity of the reactant in solution, $\Gamma$ is the surface concentration of the catalyst, $\alpha$ is the transfer coefficient of $M^{n+}$ oxidation reaction, $R$ is gas constant, $T$ is reaction temperature, $E$ is electrode potential, $E_p$ is the peak potential of $M^{n+}$ oxidation reaction, and $E_r$ is the peak potential of $M^{(n+1)+}$ oxidation reaction. Figure 47 shows the demonstrative LSV calculation at different pH, in which $k_{ap}$ was set to 10 s$^{-1}$, $v = 0.01$ V s$^{-1}$, $\Gamma = 5E^{-8}$ mol, $\alpha = 0.5$, $E_p = 1.35$ V$_{RHE}$ (pH = 14) and $E_r = 1.60$ V$_{RHE}$ (pH = 14). To further simplify the simulation, the pre-RDS reaction was defined as a 1H$^+$/1e$^-$ redox that the potential will not change with pH at the RHE scale, and all calculations do not involve changes in intermediate $pK_a$.

**PT-controlled RDS.** The RDS should be at least a 1H$^+$/1e$^-$ oxidation; thus, $E_r$ would not change with pH at the RHE scale. The pH dependence is, therefore, induced by changes in substrate concentration $[a]$. As shown in Figure 47d, the potential requirements to reach a specific current density shifted with pH values; a slope of approximately $-61$ mV pH$^{-1}$ was anticipated. Meanwhile, the reaction order of pH was calculated to be 1 at different potentials (Figure 47g).

**ET-controlled RDS.** The RDS is not related to proton transfer and also the change of proton activity, thus $[a]$ in Equation 43 is neglected; the value of $E_r$ in this case, would be constant at the NHE scale and thus changed with pH at the RHE scale ($-59$ mV pH$^{-1}$). The pH dependence is therefore induced by changes in $E_r$. As shown in Figure 47e, the relationship between potential requirements and pH exhibits a slope of $+59$ mV pH$^{-1}$; The reaction order of pH is calculated to be $-1$ at different potentials, which indicates an inverse pH effect that the reaction activity decrease when increasing the pH of electrolyte (Figure 47h).
Figure 47. Simulated LSV at different concentrations of $[\text{OH}^-]$: (a) RDS reaction is a PT step; (b) RDS reaction is an ET step; (c) RDS reaction is a CPET step. The pH-dependent OER activity at different current densities: (d) RDS reaction is a PT step; (e) RDS reaction is an ET step; (f) RDS reaction is a CPET step. The reaction order of pH at different potentials: (g) RDS reaction is a PT step; (h) RDS reaction is an ET step; (i) RDS reaction is a CPET step.

**CPET-controlled RDS.** The value of $E_r$ would not change with pH at the RHE scale, and the reaction rate was not affected by the change of proton activity since electron transfer would never be decoupled with proton transfer. Thus, the slope of the potential-pH relationship is 0 mV pH$^{-1}$, and the reaction order of pH is 0 (Figures 47f and 47i).

Referring to the concept of Pourbaix, the relationship between pH and potential requirements to reach a specific current density during catalysis was plotted in Figure 48. Reactions with ET-controlled RDS, PT-controlled RDS, and CPET-controlled RDS show significantly different slopes, which means that the properties of RDS might be identified from the linear pH dependence of activity. Under the RHE scale, a half-cell reaction that exhibits pH dependence inherently suggests the presence of decoupled proton-electron transfer pathways: a negative slope (positive reaction order) indicates the domination of proton transfer in RDS; a zero slope (zero reaction order)
suggests a concerted PCET feature of RDS; a positive slope (negative reaction order) implies that the RDS is controlled by an ET step.

**Figure 48.** (a) Schematic of proton-coupled electron transfer processes in the O-O bond formation step. The pH-dependent catalytic activity of PT, ET, and CPET steps under (b) RHE and (c) NHE scale.

### 2.4.2 Pre-RDS oxidation limited pH dependence

In practical catalysis, the pH dependence of the catalytic current may also be constrained by the pre-RDS redox. When assuming a situation that the pre-RDS oxidation $M^{n+} - e^- \rightarrow M^{(n+1)+}$ is a $2H^+ / 1e^-$ transfer process, and the RDS oxidation $M^{(n+1)+} - e^- \rightarrow M^{(n+2)+}$ is a single electron transfer process. Thus, under the NHE scale, $E_p$ would show a super-Nernst shift ($-118 \text{ mV pH}^{-1}$) with pH, and $E_r$ would be constant. It is a consensus that the value of $E_p$ must be less than that of $E_r$ (i.e., $M^{(n+1)+}$ still needs more driving force to reach a higher oxidation state of $M^{(n+2)+}$). Therefore, with the increase of $E_p$ when decreasing the pH, $E_r$ would eventually shift with pH even though it is an ET step. When reflected on the catalytic current, the current would exhibit a pH dependence for an ET-controlled RDS (Figure 49a). Figures 49b-g summarized the possible pH dependence of pre-RDS redox and catalytic current. When the slope of the pre-RDS redox is larger than that of the catalytic current, the inflection point may occur due to the constrained potential by the shifted pre-RDS redox, which makes it unreliable to conclude the properties of RDS via pH dependence of current (Figures 49b-
Therefore, additional evidence (like KIEs) would be required to screen the nature of RDS.

**Figure 49.** (a) Simulated LSV curves of catalytic events that have an ET-controlled RDS and pre-RDS oxidation with super-Nernst behavior ($2H^+/1e^-$). (b) Schematic pH response of a pre-RDS redox with a super-Nernst behavior and catalytic current with an ET-controlled RDS. (c) Schematic pH response of a pre-RDS redox with a Nernst behavior and catalytic current with an ET-controlled RDS. (d) Schematic pH response of a pre-RDS redox with a super-Nernst behavior and catalytic current with a CPET-controlled RDS. (e) Schematic pH response of a pre-RDS redox with a Nernst behavior and catalytic current with a CPET-controlled RDS. (f) Schematic pH response of a pre-RDS redox with a super-Nernst behavior and catalytic current with a PT-controlled RDS. (g) Schematic pH response of a pre-RDS redox with a Nernst behavior and catalytic current with a PT-controlled RDS.

The detailed criterion for pH dependency of OER activity is listed in **Figure 50.** Features of both pre-RDS and RDS redox would affect the determination of proton and electron transfer properties in RDS, which further affects the inference of the entire catalytic cycle. Especially for ET-controlled RDS (like radical coupling mechanism for O-O bond formation), the discussed pH-potential relationship at a constant catalytic current is only a sufficient but not necessary condition, which needs evidence for further KIE experiments to make a solid distinction.
2.5 Materials preparation

2.5.1 Synthesis of porous ITO film

Porous indium tin oxide (ITO) films were prepared by doctor-blading the paste onto ITO conducting glass using Scotch tape as a spacer, followed by sintering in an oven at 450°C for 30 min. The paste was prepared by ball milling a mixture of indium tin oxide nanoparticles (1 g), ethyl cellulose (150 mg), ethanol (8 mL), terpineol (4 mL), and acetylacetone (100 μL) for 4h.

2.5.2 Synthesis of BiVO$_4$ film

BiVO$_4$ films were fabricated following an adapted procedure from the literature.$^{348}$ In brief, 0.3675 g Bi(NO$_3$)$_3$·5H$_2$O (0.75 mmol) was dissolved in a 50 mL aqueous solution that contained 136 μL of lactic acid. After 5 minutes of ultrasonic mixing, 3.354 g (20 mmol) of KI was cautiously incorporated, and the blend was vigorously stirred for 30 min. This solution was slowly mixed with 20 mL of ethanol containing 0.1 g (0.92 mmol) of p-benzoquinone and stirred intensely for an additional 10 minutes. Nitric acid was used to adjust the final pH to 3.4, forming the BiOI deposition solution.

For the electrodeposition step, a conventional three-electrode cell was used, consisting of an FTO working electrode, a saturated Ag/AgCl reference electrode, and a Pt mesh as the counter electrode. The cathodic deposition was carried out at a potential of $-0.35$ V vs. Ag/AgCl for 20 seconds, followed by a potential of $-0.10$ V vs. Ag/AgCl for a few minutes, totaling a charge transfer of 0.37 C cm$^{-2}$.

The BiOI film underwent thermal transformation into BiVO$_4$ by being air-heated at 450°C for 2 hours (with a ramping rate of 2°C min$^{-1}$). Prior to heating, the BiOI film was coated with 40 μL of a DMSO solution containing 0.2 M VO(acac)$_2$. After cooling to room temperature, the annealed electrodes

Figure 50. Slopes of pH-activity relationship at (a) NHE scale and (b) RHE scale (question mark indicates that the slope may change over a specific pH range).
were immersed in 1.0 M NaOH for 30 minutes to remove surface V$_2$O$_5$. The resulting films were then rinsed with deionized water and dried with the air stream.

2.5.3 Synthesis of Aza-CMP

Aza-CMP employed in this thesis was synthesized following a method previously reported in the literature.$^{421}$ A mixture of 532.5 mg (1.875 mmol) of 1,2,4,5-benzenetetramine tetrahydrochloride in 15 mL of anhydrous DMF and 390 mg (1.25 mmol) of hexaketoxyoctahydrate in 5 mL of anhydrous DMF was refluxed for 48 hours under an argon atmosphere. After that, the dark brown precipitate was purified using a Soxhlet extractor with hot methanol for another 48 hours. The collected solid was then dried in a vacuum at 150°C for 24 h to obtain bulk Aza-CMP.

2.5.4 Synthesis of Aza-CMP-Co

The Aza-CMP material was modified with Co$^{2+}$ using cobalt(II) acetate. 20 mg of Aza-CMP was suspended in 10 mL of anhydrous DMF and stirred for one hour in an argon-protected environment while bubbling argon through the mixture. Separately, 85 mg of cobalt(II) acetate (1.5 equivalents to the phenanthroline units in Aza-CMP) was dissolved in another 10 mL of anhydrous DMF, also under an argon atmosphere. This cobalt(II) acetate solution was slowly added to the Aza-CMP suspension under argon, and the mixture was kept in a dispersed state by ultrasonication for 8 h at room temperature. After this, the solid was isolated by filtration and washed successively with DMF, water, methanol, and ethanol until the filtrate was clear. The final product denoted as Aza-CMP-Co, was then dried under vacuum at 80°C.

2.5.5 Preparation of Aza-CMP-Co ink and electrode.

The catalyst was dispersed into an ink solution by mixing 5 mg of the material with a 1:1 aqueous-ethanol solution, specifically comprising 0.25 mL of water and 0.25 mL of ethanol. This mixture was subsequently subjected to ultrasonic treatment for 60 minutes to ensure homogeneity. A 10 μL of the sonicated ink was then applied to a 5 mm x 5 mm carbon paper (CP) electrode. To facilitate the drying process, the electrode was maintained in an argon atmosphere until a fully dried film was achieved.

2.5.6 Synthesis of FAPbBr$_3$ photoanode

The FAPbBr$_3$ perovskite photoanode consists of two parts: the light-absorbing part (ITO/SnO$_2$/FAPbBr$_3$/carbon) and the WOC part (graphite sheet/NiFe alloy/NiFe LDH); the edge of the device is sealed with epoxy resin to prevent water degradation.
The structure of the light-absorbing part is glass/ITO/SnO$_2$/FAPbBr$_3$/carbon. ITO glass underwent a sequential cleaning process, being washed with detergent, acetone, isopropanol, and water, each for a duration of 20 minutes. Subsequently, UV/ozone (UVO) treatment was performed for 30 min to prepare the ITO substrate for use. SnO$_2$ film was then spin-coated onto the prepared ITO glass using a commercially available SnO$_2$ colloidal solution, diluted in deionized water at a 4:1 volume ratio. The spin-coating was executed at 3000 rpm for 30 seconds, after which the film was annealed on a hotplate at 150°C for 30 minutes. Once cooled, a 20-minute UVO treatment was carried out on the SnO$_2$ film before further use. The FAPbBr$_3$ film was prepared by a two-step spin-coating approach. A precursor solution containing 1.3 M of PbBr$_2$ was prepared by mixing it in a DMF and DMSO solution with a 9:1 volume ratio and stirred at 70°C overnight. This precursor was then spin-coated onto the SnO$_2$-coated substrate at 3000 rpm for 30 seconds and annealed at 70°C for 1 minute under ambient conditions. After that, 0.065 g of FABr was dissolved in 1.0 mL of methanol and spin-coated onto the existing PbBr$_2$ layer under the same conditions (3000 rpm, 30 seconds), followed by annealing at 150°C for 25 minutes in ambient air. Lastly, a carbon paste (DN-CP01) was applied onto the FAPbBr$_3$ layer using the doctor-blading method. A final annealing step was conducted in air at 100°C for 30 minutes to form a solid carbon layer on the device.

After the FAPbBr$_3$ light-absorbing part was prepared, a 160-um self-adhesive graphite sheet (GS) layer was stuck onto the carbon film (refer to step 2 in Figure 51). To enhance conductivity, the bottom edge of the attached GS layer was additionally coated with carbon paste. Subsequently, copper tape and copper wire were adhered to the ITO and GS areas, respectively (see step 3 in Figure 51). The photoanode was then sealed using the chemical-resistant epoxy resin, Loctite 9466 (step 4 in Figure 51), and allowed to cure at 60°C for 30 minutes. The devices were stored in a dry box overnight prior to further use.

The NiFe alloy catalyst layer was electrodeposited on the GS layer using a reported method with subtle modification. In brief, sodium citrate dihydrate (20.0 mmol, 6.00 g), ammonium sulfate (45.0 mmol, 6.00 g), and sodium hypophosphite monohydrate (57.0 mmol, 6.00 g) were mixed in 100 mL of deionized water at ambient temperature. Nickel(II) sulfate hexahydrate (10.0 mmol, 2.62 g) and iron(II) sulfate heptahydrate (2.0 mmol, 0.54 g) were then added into this solution while stirring. The pH of the solution was adjusted to 10.0 using a 10 M NaOH solution. A three-electrode electrochemical cell was employed for the deposition process, using a platinum mesh as the counter electrode and Ag/AgCl (saturated KCl) as the
reference electrode. The working electrode was linked to the copper wire. The cell was filled with the prepared electrodeposition solution (15 mL) and subjected to an applied potential of $-1.10 \, \text{V vs. Ag/AgCl}$ for 1600 seconds. Post-deposition, the alloy film was rinsed with deionized water and dried under an N$_2$ atmosphere for subsequent use. The NiFe LDH layer was electrochemically deposited onto the previously prepared alloy layer using an adapted method from the literature.$^{423}$ The electrolyte bath contained 5 mM nickel(II) nitrate hexahydrate and 5 mM iron(III) nitrate nonahydrate. Electrodeposition was performed at an applied potential of $-1.0 \, \text{V vs. Ag/AgCl}$ for 900 seconds. After deposition, the LDH film was cleansed using deionized water and dried in an N$_2$ atmosphere for subsequent applications. After the preparation is complete, trim the copper wire to a shorter length to reduce the possible corrosion in the electrolyte.

Figure 51. Schematic diagram of photoanode preparation in top view.
A Cobalt@Cucurbit[5]uril Complex as an Efficient Catalyst for Electrochemical and Photoelectrochemical Water Oxidation

(Paper I, Copyright 2020, Wiley-VCH)

Figure 52. Schematic diagram of the photo-driven water oxidation reaction over Co@CB[5] immobilized BiVO₄ photoanode.

PEC water splitting is a promising approach for transforming solar energy into renewable hydrogen fuels. The efficiency of water oxidation catalysis, which is crucial for generating the protons essential for hydrogen production, remains a significant challenge and a primary bottleneck in achieving water splitting. The kinetically challenging multi-electron and multi-proton reactions involved in water oxidation limited the overall performance of the semiconductor-based photoelectrochemical devices. Consequently, it is widely recognized that integrating water oxidation catalysts with semiconductor materials is indispensable for optimizing solar-driven water splitting.

Cucurbituril (CB[n]) is a set of typical macrocyclic host compounds capable of readily coordinating with metal cations due to the presence of carbonyl groups oriented toward the interior cavity of its cyclic structure. These carbonyl groups facilitate the formation of robust complexes with cations via ion-dipole interactions. Additionally, CB[n] can be either anchored or physisorbed onto metal oxide surfaces (MOₓ), allowing for the immobilization of host-guest complexes comprising CB[n] and metal cations.
onto metal oxide-based semiconductor surfaces through the remaining carbonyl groups. Notably, cobalt-based catalysts, which exhibit high OER activity under near-neutral pH conditions, are frequently paired with photoanode materials, like BiVO$_4$, to enhance the photocurrent density, reduce the onset potential, and improve the photostability. Accordingly, in this chapter, a supramolecular assembly featuring CB[5] and Co$^{2+}$ cation was selected and immobilized onto metal oxide surfaces as a heterogeneous molecular WOC (Figure 52). For the first time, this host-guest complex, when applied to porous ITO or BiVO$_4$ surfaces, demonstrated excellent electrochemical and photoelectrochemical water oxidation performance comparable to that of state-of-the-art heterogeneous WOCs, while offering a significantly more straightforward preparation procedure. These novel insights highlight the immense potential of host-guest supramolecular complexes as efficient WOCs for PEC systems.

3.1 Electrodes preparation and characterizations

The Co@CB[5] supramolecular complex was synthesized and subsequently applied to porous ITO and BiVO$_4$ substrates to assess its electrochemical and photoelectrochemical water oxidation activities. SEM characterization in Figures 53a and 53b reveals that the porous ITO substrate consists of octahedral-shaped particles, with a cross-sectional view confirming an average film thickness of approximately 1.3 μm. The porous BiVO$_4$ substrate features worm-like particles and exhibits an average film thickness of approximately 1 μm (Figures 53c and 53d).

![Figure 53. SEM images of the porous ITO substrate by (a) top view, (b) cross-sectional view. SEM images of the porous BiVO$_4$ substrate by (c) top view, (d) cross-sectional view.](image-url)
The methodology for fabricating Co@CB[5]/ITO and Co@CB[5]/BiVO4 electrodes were illustrated in Figure 54. Initially, a 1.0 mM solution of the Co@CB[5] host-guest complex was synthesized by mixing CB[5] and Co(NO3)2 in a 1:1 molar ratio. Electrospray mass spectrometry confirmed a mass-to-charge ratio (m/z) of 454.0879, aligning with the theoretical value for Co@CB[5]+H3O (m/z 454.0979) (Figure 55a). Subsequently, porous ITO and BiVO4 substrates were immersed in the Co@CB[5] solution for 30 minutes and then rinsed with deionized water, resulting in the formation of Co@CB[5]/ITO and Co@CB[5]/BiVO4 electrodes, respectively.

![Figure 54. Schematic illustration of electrode fabrication processes by immobilizing Co@CB[5] on the surface of metal oxide substrates.](image)

The corresponding FT-IR spectra exhibit blue shifts for the carbonyl groups of the CB[5] component in CB[5]/ITO, Co@CB[5]/ITO, CB[5]/BiVO4, and Co@CB[5] BiVO4 electrodes when compared to the pure CB[5] powder (Figures 55b and 55c), suggesting a strong interaction between the CB[5], Co cations, and metal oxide (MOx) substrates, thereby implying the immobilization of Co@CB[5] on the surfaces of ITO and BiVO4.429

XPS was employed to assess the surface composition and electronic states of the MOx substrate functionalized with the Co@CB[5] complex. In the high-resolution XPS spectra, when CB[5] was immobilized on the surface of MOx, a distinct N 1s signal, corresponding to the C-N bonds of CB[5], at a binding energy of 400.15 eV is evident (Figures 56a and 57a). This attests to the successful immobilization of CB[5] on the porous MOx through a simple soaking method. Moreover, upon the immobilization of Co@CB[5] on either ITO or BiVO4 substrates, a prominent Co 2p signal emerges around a binding energy of 781 eV (Figures 56b and 57b). Additionally, minor shifts from the primary N 1s signal are discernible, implying the interactions between the Co2+ center and the host ligand. It is noteworthy that the binding energies of
Co 2p in the Co@CB[5] complex diverge from those typically observed in Co-based oxides or hydroxides,\textsuperscript{430, 431} suggesting a molecular characteristic of Co@CB[5] on the MOx surfaces.

**Figure 55.** (a) Electrospray mass spectrum of the solution of Co@CB[5] host-guest complex. (b) FT-IR spectra of ITO, CB[5]/ITO, Co@CB[5]/ITO electrodes. (c) FT-IR spectra of BiVO₄, CB[5]/BiVO₄, Co@CB[5]/BiVO₄ electrodes.

**Figure 56.** High-resolution XPS spectra of ITO-based electrodes in selected (a) N 1s and (b) Co 2p areas. (c) EDS mapping images of a Co@CB[5]/ITO particle. (d) Atomic-resolution HAADF image of Co@CB[5]/ITO particle in selected small area.
Figure 57. High-resolution XPS spectra of BiVO₄-based electrodes in selected (a) N 1s and (b) Co 2p areas. (c) HRTEM image of the Co@CB[5]/BiVO₄ sample. (d) HAADF-STEM image of Co@CB[5]/BiVO₄ particle and corresponding elemental mapping images.

The surface and morphological characteristics of Co@CB[5]/ITO and Co@CB[5]/BiVO₄ samples were examined using aberration-corrected TEM. Figure 56c shows the EDS mapping images of Co@CB[5]/ITO, revealing the uniform presence of Co, N, and C elements on ITO nanoparticles. Atomic-scale HAADF image in Figure 56d indicates no structural decomposition observed after the immobilization of the Co@CB[5] complex; furthermore, neither Co oxides nor hydroxides were observed on the terminations of ITO nanoparticles post-immobilization. This finding corroborates the molecular anchoring of the Co@CB[5] complex on the ITO surface. Owing to the significantly higher atomic mass of tin and indium in bulk ITO, discerning individual cobalt molecular complexes on the ITO surface through atomic resolution HAADF images remains challenging. Additionally, EDS analysis in selected areas yields a metal composition ratio of Co/In/Sn as approximately 1.03 : 91.97 : 7.8, aligning with the extent of surface mono-molecular layer distribution for Co components. The interface morphology of Co@CB[5]/BiVO₄ was probed using high-resolution transmission electron microscopy (HRTEM), as shown in Figure 57c, which shows no obvious metal oxide films or nanoparticles covering the surface of BiVO₄ nanoparticles. Regrettably, atomic resolution STEM could not provide detailed structural information for the surface of Co@CB[5]/BiVO₄ due to electron beam-induced surface damage to BiVO₄ when exposed to the focused high-energy electron beam. HAADF-STEM and the corresponding EDS mapping images demonstrate that the Co, N, and C elements in the Co@CB[5] complex are uniformly distributed on the BiVO₄ nanoparticle.
surfaces (Figure 57d). All the above findings suggest molecular-level immobilization of Co@CB[5] on the MOx surfaces.

3.2 Electrochemical-driven water oxidation

To evaluate the water oxidation performance of the Co@CB[5]/ITO electrode, LSV measurements were conducted at 25°C using a standard three-electrode cell with 1.0 M borate buffer solution (pH 9.2) as the electrolyte. As shown in Figure 58a, both the ITO substrate and the CB[5]/ITO electrode exhibit negligible OER activity. Conversely, the anodic current density of the Co@CB[5]/ITO electrode increases sharply beyond a modest onset potential of 1.05 V vs. NHE, further escalating at higher potentials. A current density of 1.0 mA cm\(^{-2}\) is achieved at an overpotential of 485 mV. For comparative purposes, a Co/ITO electrode was fabricated by immersing ITO in a 1.0 mM Co\(^{2+}\) solution for 30 minutes. This Co/ITO electrode exhibits significantly lower anodic current density compared to the Co@CB[5]/ITO electrode. Linear fitting for the LSV curve of Co@CB[5]/ITO electrode gives a Tafel slope of 59.5 mV dec\(^{-1}\) (Figure 58b).

Steady-state catalytic activities were ascertained through chronopotentiometry measurements. The Co@CB[5]/ITO electrode necessitates only 1.23 V and 1.29 V vs. NHE to achieve current densities of 1.0 mA cm\(^{-2}\) and 2.5 mA cm\(^{-2}\), respectively (Figure 58c). The overpotential remains stable throughout the measurements, highlighting the stability of Co@CB[5]/ITO in OER. Quantification of the electrochemically generated oxygen was confirmed via GC, revealing that 8.62 μmol of O\(_2\) is produced when a total charge of 3.6 C is passed through the electrode, corresponding to a Faraday efficiency of 92.6% (Figure 59b).

The effective surface coverage of Co\(^{2+}\) on the ITO substrate was quantified based on the linear correlation between the peak current of Co\(^{2+/3+}\) oxidation and the scan rate. The calculated surface coverage was 4.54×10\(^{-9}\) mol cm\(^{-2}\), and this order of magnitude aligns with those of molecule immobilized porous surface (Figure 59a).\(^{227}\) The total Co\(^{2+}\) loading was confirmed through ICP-OES, revealing a value of 4.98×10\(^{-9}\) mol cm\(^{-2}\), marginally higher than the redox-active Co\(^{2+}\). TOFs were calculated from the Co\(^{2+}\) loading and LSV data acquired at a low scan rate of 10 mV s\(^{-1}\). The logarithm of the TOFs demonstrates a linear relationship with the applied overpotentials ranging from 460 mV to 550 mV, as illustrated in Figure 58d. A TOF of 0.3 s\(^{-1}\) is achieved at \(\eta = 460\) mV, reaching 9.9 s\(^{-1}\) at \(\eta = 550\) mV. Table 2 lists the performance benchmark of the Co@CB[5]/ITO electrode in comparison to previously reported electrodes for water oxidation in near-neutral conditions, including molecular and inorganic material catalysts immobilized on conducting glass substrates. This comparison substantiates
that the Co@CB[5]/ITO electrode ranks among the top-performing OER anodes in terms of overpotential, current density, and TOF.

**Figure 58.** (a) LSV curves of Co@CB[5]/ITO and comparison electrodes in 1.0 M borate buffer (pH 9.2) at a scan rate of 50 mV s\(^{-1}\). (b) Tafel plot of Co@CB[5]/ITO. (c) Chronopotentiometric measurement of OER at current densities of 1.0 and 2.5 mA cm\(^{-2}\) for 5 h without IR compensation. (d) TOFs of Co@CB[5]/ITO at various overpotentials.

**Figure 59.** (a) LSV curves of Co@CB[5]/ITO electrode at different scan rates in a 0.1 M nBt4NPF\(_6\) acetonitrile solution. Inset: dependence of peak current density on different scan rates (the calculated loading amounts of redox-active cobalt is 4.54×10\(^{-9}\) mol cm\(^{-2}\)). (b) The Faradaic efficiency of Co@CB[5]/ITO electrode for OER in 1.0 M borate buffer. The value was determined by comparing the measured amount of oxygen gas and the theoretical value calculated based on the
transferred charge. Oxygen evolution was detected by gas chromatography, and the quantitative yield of 92.6% was obtained at \( j = 1.0 \text{ mA cm}^{-2} \).

**Table 2.** Water oxidation performance of recently published catalysts immobilized on conducting glass substrates.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Immobilization method</th>
<th>Electrolyte</th>
<th>( \eta ) (mV at ( j = 1 \text{ mA cm}^{-2} ))</th>
<th>TOF (h(^{-1}) at ( \eta = 530 \text{ mV} ))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co@CB[5]</td>
<td>Soaking</td>
<td>1.0 M KBi (pH 9.2)</td>
<td>480</td>
<td>15120 (4.2 s(^{-1}))</td>
<td>This work</td>
</tr>
<tr>
<td>Fe-based</td>
<td>Electro-deposition</td>
<td>0.1 M Pi (pH 7.0)</td>
<td>480</td>
<td>756</td>
<td>433</td>
</tr>
<tr>
<td>MnCat</td>
<td>Electro-deposition</td>
<td>0.1 M Pi (pH 7.0)</td>
<td>590</td>
<td>36</td>
<td>434</td>
</tr>
<tr>
<td>Co-based</td>
<td>Electro-deposition</td>
<td>0.1 M Pi (pH 7.0)</td>
<td>550</td>
<td>61.2</td>
<td>130</td>
</tr>
<tr>
<td>[Co(IDA)(_2)]</td>
<td>Electro-deposition</td>
<td>0.6 M NaBi (pH 9.2)</td>
<td>~425</td>
<td>N/A</td>
<td>435</td>
</tr>
<tr>
<td>[Co(NTA)(O(_2)H(_2))(_2)]</td>
<td>Electro-deposition</td>
<td>0.6 M NaBi (pH 9.2)</td>
<td>~450</td>
<td>N/A</td>
<td>435</td>
</tr>
<tr>
<td>Mn(_3)(PO(_4))(_2)</td>
<td>Precipitation</td>
<td>0.5 M Pi (pH 7.0)</td>
<td>680 (0.32 mA cm(^{-2}))</td>
<td>4.4 (680 mV)</td>
<td>436</td>
</tr>
<tr>
<td>LiMn(_2)O(_7)</td>
<td>Solid-state synthesis</td>
<td>0.5 M Pi (pH 7.0)</td>
<td>680 (0.5 mA cm(^{-2}))</td>
<td>4.2 (680 mV)</td>
<td>437</td>
</tr>
<tr>
<td>NiO(_x)-en</td>
<td>Electro-deposition</td>
<td>0.1 M NaBi (pH 9.2)</td>
<td>510</td>
<td>54 (610 mV)</td>
<td>438</td>
</tr>
<tr>
<td>Cu-Bi</td>
<td>Electro-deposition</td>
<td>0.2 M Bi (pH 9.0)</td>
<td>576</td>
<td>N/A</td>
<td>439</td>
</tr>
</tbody>
</table>

### 3.3 Photoelectrochemical-driven water oxidation

The photoelectrochemical water oxidation performance of the Co@CB[5]/BiVO\(_4\) photoanode was assessed using LSV at a scan rate of 10 mV s\(^{-1}\). As illustrated in **Figure 60a**, the photocurrent density of the pristine BiVO\(_4\) at 1.23 V vs. RHE is approximately 1.8 mA cm\(^{-2}\); when sulfite is introduced as a hole scavenger, this value increases to 5.4 mA cm\(^{-2}\). Upon immobilizing Co@CB[5] onto the BiVO\(_4\) surface, the resultant Co@CB[5]/BiVO\(_4\) photoanode exhibits a photocurrent density of 4.8 cm\(^{-2}\) under identical conditions but without the use of sulfite as a hole scavenger. For comparison, BiVO\(_4\) immersed in a Co\(^{2+}\) solution for 30 minutes (Co/BiVO\(_4\)) yields a photocurrent density of only 2.3 mA cm\(^{-2}\) at the same potential. The ABPE was derived from the corresponding LSV curve (**Figure 60b**), revealing a maximum ABPE of 1.79% at 0.60 V vs. RHE for the Co@CB[5]/BiVO\(_4\) electrode, which is 5.5 times higher than that of the unmodified BiVO\(_4\) (0.32%). The IPCE of Co@CB[5]/BiVO\(_4\) exceeds 87% below 450 nm, whereas the respective IPCE values for BiVO\(_4\) and Co@CB[5]/BiVO\(_4\) are approximately 35% and 88% at 420 nm (1.23 V vs. RHE) (**Figure 60c**). These results underscore the superior photon-to-current conversion efficiency of the Co@CB[5]/BiVO\(_4\) photoanode assembled through host-guest interactions.
Figure 60. (a) LSV curves of Co@CB[5]/BiVO4, Co/BiVO4, BiVO4, and BiVO4 with the hole scavenger Na2SO3 in 1 M borate buffer (scan rate: 10 mV s−1). (b) ABPEs of Co@CB[5]/BiVO4 and BiVO4 that calculated from LSV curves. (c) IPCEs of Co@CB[5]/BiVO4 and BiVO4. (d) Light response of Co@CB[5]/BiVO4 and pristine BiVO4 photoanodes under chopped irradiation at a constant bias of 0.6 V vs. RHE.

Under chopped-light exposure, the unmodified BiVO4 yields a modest photocurrent density of less than 0.25 mA cm⁻² at a constant applied potential of 0.6 V vs. RHE (Figure 60d). In contrast, the Co@CB[5]/BiVO4 photoanode achieves a significantly higher photocurrent density, approximately 2.4 mA cm⁻², highlighting the crucial role of Co@CB[5] in the water oxidation kinetics. Upon long-term photolysis at 0.6 V vs. RHE under continuous irradiation, the photocurrent density of the Co@CB[5]/BiVO4 photoanode gradually declines from 2.5 to 2.3 mA cm⁻² over 30 minutes (Figure 61a). The photogenerated oxygen in the headspace was quantified using GC. Given the four-electron process for oxygen evolution, the electron flux through the electrode correlated well with the measured oxygen, resulting in a Faradaic efficiency of 90.3% for the Co@CB[5]/BiVO4 photoanode (Figure 61b). The photocurrent density and the maximum ABPE achieved by Co@CB[5]/BiVO4 are compared against previously reported systems, with the results detailed in Table 3. Remarkably, the Co@CB[5]/BiVO4 photoanode outperforms most catalyst-modified,
undoped BiVO₄ counterparts in both metrics. This host-guest complex-assembled photoanode offers the advantage of avoiding tedious organic synthesis. Additionally, the high catalytic activity of Co@CB[5] suggests its viability as a substitute for state-of-the-art metal oxides and molecular catalysts in solar fuel applications.

Figure 61. (a) The i-t curve of Co@CB[5]/BiVO₄ photoanode at a constant applied potential of 0.6 V vs. RHE. (b) The Faradaic efficiency of Co@CB[5]/BiVO₄ photoanode. Oxygen evolution was detected by gas chromatography, and the charge passed during the photolysis of Co@CB[5]/BiVO₄ photoanode at an applied potential of 0.6 V vs. RHE. Measurement was carried out in a 1.0 M borate buffer (pH 9.2) under AM 1.5G simulated sunlight irradiation (100 mW cm⁻²).

Table 3. PEC performance of reported BiVO₄-based photoanodes.

<table>
<thead>
<tr>
<th>Photoanode</th>
<th>Immobilization method</th>
<th>Electrolyte</th>
<th>Photocurrent density (1.23 VRHE)</th>
<th>Max ABPE (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co@CB[5]/BiVO₄</td>
<td>Soaking</td>
<td>1.0 M KBi (pH 9.2)</td>
<td>4.8 mA cm⁻²</td>
<td>1.79</td>
<td>This work</td>
</tr>
<tr>
<td>Co₄O₄ Cubane/BiVO₄</td>
<td>Drop casting</td>
<td>0.5 M NaBi (pH 9.3)</td>
<td>5 mA cm⁻²</td>
<td>1.8</td>
<td>339</td>
</tr>
<tr>
<td>ultrathin CoOOH/BiVO₄</td>
<td>Plasma-exfoliation</td>
<td>0.2 M Na₂SO₄ (pH=7.0)</td>
<td>4.9 mA cm⁻²</td>
<td>0.85</td>
<td>440</td>
</tr>
<tr>
<td>FeCoO₂/BiVO₄</td>
<td>Photo-electrodeposition</td>
<td>1.0 M KBi (pH 9.5)</td>
<td>4.8 mA cm⁻²</td>
<td>1.16</td>
<td>441</td>
</tr>
<tr>
<td>Co-Cubanes/pGO/LDH/BiVO₄</td>
<td>Soaking</td>
<td>1.0 M KBi (pH 9.0)</td>
<td>4.5 mA cm⁻²</td>
<td>2.0</td>
<td>442</td>
</tr>
<tr>
<td>NiOOH/FeOOH/BiVO₄</td>
<td>Photo-electrodeposition</td>
<td>0.5 M KPi (pH 7.0)</td>
<td>4.5 mA cm⁻²</td>
<td>1.75</td>
<td>443</td>
</tr>
<tr>
<td>NiFeO₂-Bi/BiVO₄</td>
<td>Photo-electrodeposition</td>
<td>1.0 M KBi (pH 9.3)</td>
<td>4.3 mA cm⁻²</td>
<td>2.02</td>
<td>316</td>
</tr>
<tr>
<td>Co-salophen@Nafion/BiVO₄</td>
<td>Drop casting</td>
<td>0.1 M KPi (pH 7.0)</td>
<td>4.3 mA cm⁻²</td>
<td>1.18</td>
<td>444</td>
</tr>
<tr>
<td>NiOOH/NiO/CoO₂/BiVO₄</td>
<td>Atomic layer deposition</td>
<td>0.1 M KPi (pH 7.0)</td>
<td>3.5 mA cm⁻²</td>
<td>1.5</td>
<td>305</td>
</tr>
<tr>
<td>CoMOF/BiVO₄</td>
<td>Drop casting/soaking</td>
<td>0.5 M Na₂SO₄</td>
<td>3.1 mA cm⁻²</td>
<td>0.9</td>
<td>445</td>
</tr>
<tr>
<td>CoTCPP/Al₂O₃/BiVO₄</td>
<td>Soaking</td>
<td>0.1 M Na₂SO₄ (pH 6.8)</td>
<td>2.1 mA cm⁻²</td>
<td>0.45</td>
<td>328</td>
</tr>
<tr>
<td>[(cy)Ru(L₂bpy)OH₂]+/BiVO₄</td>
<td>Soaking</td>
<td>0.1 M KPi (pH 7.1)</td>
<td>1.3 mA cm⁻²</td>
<td>N/A</td>
<td>337</td>
</tr>
</tbody>
</table>
Post-characterization of the electrodes following OER tests is essential to corroborate the reaction mechanism and confirm the stability of the as-fabricated electrodes. XPS was employed to analyze the composition and electronic states of the Co@CB[5]/ITO and Co@CB[5]/BiVO₄ samples post-OER (Figures 62a-d). The binding energies for both N 1s and Co 2p in Co@CB[5]/ITO and Co@CB[5]/BiVO₄ remain consistent with their pre-OER values, demonstrating the stability of Co@CB[5] during OER. Moreover, FT-IR spectra reveal that Co@CB[5] is maintained on the electrode surfaces post-OER (Figures 62e and 62f). Integrating these findings, it is evident that Co@CB[5] retains its supramolecular architecture and exhibits stability throughout the OER process.

Figure 62. XPS spectra of pristine and tested Co@CB[5]/ITO in selected (a) N 1s and (b) Co 2p area. XPS spectra of pristine and tested Co@CB[5]/BiVO₄ in selected (c) N 1s and (d) Co 2p area. FT-IR spectra of (a) Co@CB[5]/ITO and (b) Co@CB[5]/BiVO₄ before and after the OER measurements.
3.4 **Kinetic insights**

Electrochemical impedance spectroscopy (EIS) was employed to investigate charge transport behavior in the interface of the electrodes. As shown in **Figure 63a**, semicircles for Co@CB[5]/BiVO₄ and BiVO₄ electrodes fit well with Randles equivalent circuit model. The charge-transfer resistance (R_{ct}) values, obtained from the semicircle diameters, served as estimates for charge transport at the photoanode-electrolyte interface. Remarkably, under illumination at 0.6 V vs. RHE, the Co@CB[5]/BiVO₄ electrode displays a significantly lower R_{ct} value (96 Ω) compared to bare BiVO₄ (303 Ω), highlighting its superior hole-transfer capabilities at the interface.

**Figure 63.** (a) EIS of BiVO₄ and Co@CB[5]/BiVO₄ photoanodes measured under 0.6 V vs. RHE and AM 1.5G (100 mW cm⁻²) in 1.0 M borate buffer (pH 9.2). (b) LSV curves of Co@CB[5]/ITO in anhydrous sodium borate H₂O and D₂O solutions. Inset: the KIEs against potential. LSV curves of (c) Co@CB[5]/BiVO₄ and (d) BiVO₄ in anhydrous sodium borate H₂O and D₂O solutions under light irradiation. Inset: the corresponding KIEs against potential.

The charge transfer efficiency is governed by the water oxidation kinetics and the rate of charge recombination on the surface of BiVO₄. KIEs serve as valuable indicators of proton transfer in water oxidation and facilitate the elucidation of the RDS in the catalytic cycle. As evidenced in **Figure 63b**, the KIE value for the Co@CB[5]/ITO electrode exceeds 2.0, suggesting that O-H bond cleavage is involved in the RDS of electrochemical-driven water
oxidation, further implying a water nucleophilic attack mechanism. Upon anchoring Co@CB[5] onto the surface of BiVO₄, the KIE value for the Co@CB[5]/BiVO₄ photoanode hovers around 1.0 as the applied bias increased, signifying that O-H bond cleavage is not involved in the RDS for photo-driven water oxidation (Figure 63c). Conversely, the KIE value for the bare BiVO₄ photoanode is approximately 1.5, implicating proton transfer as a key process in its RDS (Figure 63d). Therefore, the immobilization of Co@CB[5] onto BiVO₄ significantly enhances proton transfer kinetics, thereby shifting the RDS to a process that does not involve proton transfer. This underscores the pivotal role of Co@CB[5] in enhancing the efficiency of light-driven water oxidation in assembling photoanodes.

**Figure 64.** IMPS spectra of (a) BiVO₄ and (b) Co@CB[5]/BiVO₄ at various potentials. The rate constants for (c) charge recombination ($k_{rec}$) and (d) charge transfer ($k_{trans}$) were extracted from IMPS spectra.

The kinetics of charge transfer and surface recombination were systematically evaluated using IMPS to elucidate the specific role of Co@CB[5] in the BiVO₄ system. Figures 64a and 64b show representative IMPS responses for both bare BiVO₄ and Co@CB[5]/BiVO₄ photoanodes in the complex plane. The IMPS spectrum features two semicircles located in the 4th and 1st quadrants, which are attributed to resistance-capacitance attenuation and the interplay between charge transfer and recombination,
respectively.\textsuperscript{447} Interestingly, the upper semicircle for BiVO$_4$ shows minimal variation upon increasing the applied potential (Figure 64a), and the recombination rate constant $k_{\text{rec}}$ remains relatively constant across varying potentials (Figure 64c). This observation suggests significant charge recombination in the BiVO$_4$ photoanode over a broad potential range. Conversely, the upper semicircle for the Co@CB[5]/BiVO$_4$ photoanode shrinks with rising potential (Figure 64b), and $k_{\text{rec}}$ diminishes by factors ranging from 6.5 to 30 across the entire potential range subsequent to Co@CB[5] functionalization. Additionally, Figure 64d reveals that the charge transfer rate constant $k_{\text{trans}}$ for Co@CB[5]/BiVO$_4$ surpasses that of BiVO$_4$ at all potentials. Specifically, at 0.6 V vs. RHE, $k_{\text{trans}}$ for Co@CB[5]/BiVO$_4$ is fourfold that of BiVO$_4$.

Employing sodium sulfite (Na$_2$SO$_3$) as a hole scavenger, rapid oxidation kinetics and minimal surface recombination were anticipated. As illustrated in Figure 65a, the surface charge transfer efficiency ($\eta_{\text{surface}}$) at the electrode-electrolyte interface was obtained using Equation 41 and data from Figure 60a. This approach results in an outstanding $\eta_{\text{surface}}$ of 80\% for Co@CB[5]/BiVO$_4$ at 0.8 V vs. RHE, which is significantly higher than the 15\% observed for bare BiVO$_4$. Notably, the values of $\eta_{\text{surface}}$, derived from IMPS results, align with those determined from $J$-$V$ curves, confirming the accuracy of our findings (Figure 65b). These results clearly confirm that Co@CB[5] acts not merely as a passivation agent but as an effective molecular catalyst that both accelerates the water oxidation reaction and inhibits surface charge recombination in the BiVO$_4$ system.

![Figure 65](image.png)

**Figure 65.** Surface charge transfer efficiency of the BiVO$_4$ and Co@CB[5]/BiVO$_4$ photoanodes obtained from (a) the $J$-$V$ plots of water oxidation and sulfite oxidation and (b) IMPS analysis.

### 3.5 Conclusions

The host-guest supramolecular complex Co@CB[5], working as a molecular WOC, was successfully immobilized on porous ITO and BiVO$_4$ substrates.
When anchoring onto porous ITO, the Co@CB[5] complex exhibits high electrochemical activity for water oxidation. The fabricated Co@CB[5]/ITO electrode yields a TOF of 9.9 s$^{-1}$ at an overpotential of 550 mV in a pH 9.2 borate buffer, while maintaining robust stability. In the meantime, when Co@CB[5] is grafted onto the surface of porous BiVO$_4$, an n-type semiconductor, the resultant Co@CB[5]/BiVO$_4$ photoanode demonstrates exceptional PEC performance with a high photocurrent density of 4.8 mA cm$^{-2}$ at 1.23 V vs. RHE under illumination of 100 mW cm$^{-2}$ (AM 1.5G). Based on the reaction kinetics analyzed using EIS, KIEs, and IMPS, the role of Co@CB[5] on BiVO$_4$ is summarized in Figure 66. In the case of bare BiVO$_4$, photo-generated holes can either participate directly in water oxidation (pathway 1) or recombine with surface-trapped electrons (pathway 2). The low intrinsic water oxidation activity of BiVO$_4$ results in proton transfer-limited hole injection to the electrolyte, thereby exhibiting primary KIEs. Conversely, the immobilization of Co@CB[5] on the BiVO$_4$ surface leads to enhanced OER activity. This enhancement benefits from the efficient transfer and utilization of photo-generated holes for water oxidation (pathway 3). Simultaneously, the accelerated consumption of these holes minimizes the recombination probability with photo-generated electrons, thereby elevating the charge transfer efficiency of Co@CB[5]/BiVO$_4$ compared to bare BiVO$_4$. The Co@CB[5] host-guest complex demonstrates exceptional performance in both electrochemical and photoelectrochemical water oxidation, offering new opportunities for developing supramolecular complexes as versatile catalysts, potentially extendable to other catalytic processes.

*Figure 66. Schematic illustration of the elementary processes in (a) BiVO$_4$ and (b) Co@CB[5]/BiVO$_4$ photoanodes. The transfer of holes that were generated from photo-induced charge separation have three pathways at the semiconductor-electrolyte interface (solid lines: majority events; dotted lines: minority events): (1) direct water oxidation with low $k_{\text{trans}}$, (2) surface charge recombination, and (3) charge transfer via Co@CB[5] with high $k_{\text{trans}}$.*/
4. Intramolecular Hydroxyl Nucleophilic Attack Pathway by a Polymeric Water Oxidation Catalyst with Single Cobalt Sites

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Figure 67. Schematic diagram of the water oxidation reaction over Aza-CMP-Co under alkaline conditions.

A comprehension of the water oxidation mechanism and the structure-activity relationships of catalysts is crucial for the advancement of sophisticated catalytic systems. Molecular WOCs, characterized by their well-defined structures, have garnered significant interest due to their facile tunability of structural and electronic properties, as well as their capability to facilitate multiple proton-electron transfer reactions. These features have made them ideal candidates for in-depth mechanistic studies. However, cumbersome synthesis and immobilization, along with their inherent instability, have constrained their broader applications. On the other hand, transition metal-based heterogeneous catalysts offer enhanced durability but suffer from an incomplete understanding of the water oxidation mechanism and structure-activity correlations. This is further complicated by the
presence of multiple catalytic sites within a single catalyst sample, which obscures the mechanistic elucidation of heterogeneous WOCs.\textsuperscript{449}

The presence of mixed mechanisms within a single reaction system can obfuscate the interpretation and assignment of experimental kinetic results. Consequently, a catalytic system capable of delivering definite coordination environments to establish structurally well-defined transition-metal active sites becomes imperative for reliable mechanistic studies of heterogeneous WOCs. Aza-CMP, synthesized via the polycondensation of 1,2,4,5-benzenetetramine tetrahydrochloride and triquinoyl octahydrate, contains an array of uniformly distributed, periodic pyridinic nitrogen coordination sites. Unlike 2D graphene-based SACs, which exhibit a variety of binding modes, Aza-CMP incorporates solely pyridinic nitrogen functionality.\textsuperscript{450} Its robust, microporous structure ensures both high chemical stability and excellent electrical conductivity, serving as an ideal foundation for the development of transition metal-grafted heterogeneous catalysts characterized by uniform chemical environments and minimal structural deviation.\textsuperscript{451, 452} This chapter explores the synthesis and characterization of Aza-CMP coordinated single cobalt sites as a heterogeneous WOC (Figure 67). The single cobalt sites in Aza-CMP-Co demonstrate exceptional activity under both alkaline and near-neutral conditions. Furthermore, the well-defined molecular nature of the isolated catalytic sites renders Aza-CMP-Co a reliable model for investigating the mechanisms underlying heterogeneous water oxidation. This chapter offers a comprehensive understanding of the pivotal role that electrolyte pH plays in water oxidation catalysis, as well as the enhancement of water oxidation activity by regulating the intramolecular hydroxyl nucleophilic attack (IHNA) pathway.

4.1 Physical characterizations of Aza-CMP and Aza-CMP-Co

The chemical composition and structure of the synthesized Aza-CMP (Figure 68) were confirmed by multiple techniques. The solid-state $^{13}$C CP-MAS NMR spectrum shows two distinct peaks, each corresponding to chemically non-equivalent carbon atoms within the polymer structure (Figures 69a and 69b). These spectral features concur with prior findings in the literature.\textsuperscript{453} The FT-IR spectrum reveal characteristic absorption bands at 1600, 1470, and 1250 cm$^{-1}$, which can be assigned to C=C symmetric stretching, C-C vibrations in aza-aromatic rings, and C=N symmetric vibrations, respectively (Figure 69c). Elemental analysis corroborates these findings, yielding a C/N/H weight ratio of 52.8: 23.6: 2.8, consistent with literature data.\textsuperscript{421} Powder XRD analysis demonstrates a pronounced diffraction peak at 27.09°, indicative of the layered structure of the Aza-CMP with an interlayer spacing (d-spacing) of 0.329 nm (Figure 69d).
Figure 68. The chemical structure of Aza-CMP.

Figure 69. (a) Solid-State $^{13}$C CP/MAS NMR results of Aza-CMP. Three signals correspond to the three different carbon atoms observed in the polymer (* = sidebands of main peaks). (b) Structure of three different carbon atoms in Aza-CMP. (c) FT-IR spectrum of Aza-CMP. (d) Powder XRD pattern of Aza-CMP.
The AFM topographic image shows a nanolayered Aza-CMP (minimum height of about 4 nm) over micron-length dimensions (Figure 70a). The STM image clearly reveals the distributed holey structure, uniformly organized in hexagonal arrays with inter-hole distances measuring around 1.1 nm (Figure 70b). Further analysis of the topographic height profiles indicates an absence of sub-nanostructures within these holes, corroborating an AA eclipsed stacking configuration (Figure 70c). Field-emission SEM further elucidates the bulk morphology of Aza-CMP, revealing a distinct microporous structure under high magnification (Figure 71a). EDS mapping substantiates the homogeneous distribution of carbon and nitrogen atoms throughout the material (Figure 71b). Collectively, these characterizations affirm the successful synthesis of the Aza-CMP building block.

Figure 70. (a) AFM topographic image of Aza-CMP and corresponding height profiles. (b) Atomic-resolution STM topographic image of the Aza-CMP and corresponding height profile. (c) Possible stacked models.
Subsequent to Aza-CMP synthesis, Aza-CMP was treated with cobalt(II) acetate under ultrasonic conditions to incorporate cobalt ions into the CMP matrix (Figure 72a). The total Co$^{2+}$ content in the resulting Aza-CMP-Co was quantified at 1.86 wt%, equivalent to a cobalt loading of $10^{-7}$ mol/mg$_{Aza-CMP}$. A comprehensive characterization of the complexation structure Co$^{2+}$ and Aza-CMP was conducted employing multiple analytical techniques. High-resolution XPS spectrum covering the Co 2p region displays doublet peaks centered at approximately 781.2 eV ($2p_{3/2}$) and 796.7 eV ($2p_{1/2}$), accompanied by three satellite features, corresponding to Co$^{2+}$ complexes with nitrogen ligands rather than cobalt oxides (Figure 72b). Moreover, the powder XRD pattern for Aza-CMP-Co corroborates the retention of the original layered framework structure post the Co$^{2+}$ immobilization (Figure 72c). The porous nature of both Aza-CMP and Aza-CMP-Co was confirmed through nitrogen adsorption-desorption isotherms measured at 77 K (Figure 72d). The pore size is found to be around 1.36 nm, aligning closely with literature values for Aza-CMP (1.37 nm). Solid-state $^{13}$C CP-MAS NMR spectroscopy reveals that the paramagnetic Co$^{2+}$ broadened the NMR peaks, but peaks attributable to the CMP matrix remain identifiable (Figure 73a). FT-IR spectra indicate the persistence of characteristic C-C, C=C, and C=N vibrational peaks after Co$^{2+}$ binding (Figure 73b). A noticeable blue shift in the C=N and C=C vibration and a reduction in the intensity of the C-C vibration are observed with cobalt loading, confirming alterations in the local coordination environment of the framework.
Figure 72. (a) Chemical structure of Aza-CMP-Co. (b) High-resolution XPS spectrum of Aza-CMP-Co for Co 2p region. (c) Powder XRD spectra of Aza-CMP and Aza-CMP-Co. (d) N₂ adsorption-desorption isotherms of Aza-CMP and Aza-CMP-Co (STP = standard temperature and pressure). Inset: corresponding pore size distributions obtained using the NLDFT method.

Figure 73. (a) Solid-state \(^{13}\)C CP-MAS NMR spectra and (b) FT-IR spectra of Aza-CMP and Aza-CMP-Co.

The valence states and local bonding symmetries of the as-synthesized Aza-CMP-Co were investigated using XAS. The XANES profile for Aza-CMP-Co deviates significantly from those of Co foil, CoO, and Co₂O₃, indicative of the distinct coordination environments (Figure 74a). The normalized Co K-edge absorption threshold in the as-synthesized catalysts closely aligns
with that of CoO, suggesting an approximate cobalt valence state of +2. Additionally, the subdued intensity of the pre-edge peak at 7710.4 eV implies a broken square-planar geometry and the presence of axial ligands.\textsuperscript{458} EXAFS analysis was performed to further elucidate the coordination configurations of the as-synthesized catalysts (Figure 74b). The primary peak, centered approximately at 1.65 Å, is attributable to Co-N/O scattering pathways. The absence of second-shell region peaks, commonly observed in reference samples, substantiates the exclusive formation of single-site cobalt in Aza-CMP-Co. Correspondingly, WT analysis of the EXAFS data for Aza-CMP-Co reveals an intensity maximum at 3.90 Å\textsuperscript{-1}, indicating the presence of mononuclear cobalt centers (Figure 74c). The subsequent least-squares fitting of the EXAFS spectrum in R-space yielded quantitative structural parameters (Figure 74d). Employing Co-N and Co-O scattering pathways based on DFT models, the primary peak at 1.65 Å is deduced to arise from two distinct paths with bond lengths of 2.00 and 2.10 Å. The shorter path is ascribed to Co-N bonds with a coordination number constrained to 2, while the longer path is attributed to Co-O bonds originating from adsorbed hydroxyl or water groups. The resulting coordination number for the longer Co-O path is fitted to be 3.8 (Table 4), thereby revealing a Co-N\textsubscript{2}/O\textsubscript{4} motif, as structurally illustrated in Figure 72a.

**Table 4.** Co K-edge EXAFS curve fitting parameters\textsuperscript{a} of Aza-CMP-Co.

<table>
<thead>
<tr>
<th>Path</th>
<th>(d^b) (Å)</th>
<th>N</th>
<th>(R) (Å)</th>
<th>(\sigma^2) (Å\textsuperscript{2})</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-N</td>
<td>1.98</td>
<td>2</td>
<td>2.00 ± 0.07</td>
<td>0.004 ± 0.001</td>
<td>0.008</td>
</tr>
<tr>
<td>Co-O</td>
<td>2.16</td>
<td>3.8 ± 0.6</td>
<td>2.10 ± 0.03</td>
<td>0.004 ± 0.001</td>
<td></td>
</tr>
</tbody>
</table>

\(a\) N, coordination number; \(R\), the distance between absorber and backscatter atoms; \(\sigma^2\) Debye-Waller factor to account for thermal and structural disorders; R-factor, indicates the goodness of the fit. \(S_0^2\) was fixed to 0.9 according to reference Co foil fitting. Data range: 2.5 \(\leq k \leq 12\) Å\textsuperscript{-1}, 1 \(\leq R \leq 3\) Å. \(b\) The distances for Co-N and Co-O are from the calculated DFT model of Aza-CMP-Co. \(c\) These coordination numbers were constrained as N(Co-N) = 2 based on the DFT model of Aza-CMP-Co.
The morphology of Aza-CMP-Co was studied by AFM, SEM, and TEM. As shown in Figure 75c, AFM imaging reveals a well-defined layered structure with a thickness of approximately 4 nm, which suggests that the inherent layered structure of the CMP matrix remains unaltered upon the Co$^{2+}$ complexation. SEM images of Aza-CMP-Co presented in Figure 75b demonstrate no discernible morphological alterations compared to those of Aza-CMP (Figure 71a). The atomic-resolution HAADF-STEM image reveals the presence of isolated single metal sites, with the bright dots in Figure 75a indicating the atomic dispersion of cobalt ions without nanoparticle aggregation. Furthermore, the Z-contrast HAADF image, accompanied by EDS elemental mapping images, corroborates the uniform distribution of Co, C, N, and O elements within the nano-porous 2D-CMP framework, devoid of aggregation (Figure 75d).
Figure 75. (a) Atomic-resolution HAADF-STEM image of Aza-CMP-Co (red circles indicate single molecular sites). (b) SEM images of Aza-CMP-Co. (c) AFM topographic image of Aza-CMP-Co and corresponding height profiles along the lines. (d) HAADF-STEM and elemental mapping images of Aza-CMP-Co.

4.2 Water oxidation electrocatalysis

The electrocatalytic water oxidation performance of Aza-CMP-Co was investigated in a 1.0 M NaOH solution, utilizing a carbon paper electrode with a mass loading of 0.4 mg cm$^{-2}$ (Aza-CMP-Co/CP). For comparative analysis, a standard Co(OH)$_2$ catalyst was electrodeposited onto a CP
substrate (Co(OH)_2/CP), while an unmodified Aza-CMP/CP sample served as a control. The Aza-CMP-Co/CP electrode demonstrates an onset potential of 1.48 V (quantified at a current density of 0.1 mA cm\(^{-2}\)), which contrasts with 1.58 V observed for Co(OH)_2/CP (Figure 76a). Tafel slopes of approximately 44 mV dec\(^{-1}\) for Aza-CMP-Co/CP and 65.4 mV dec\(^{-1}\) for Co(OH)_2/CP, indicating a distinctive water oxidation pathway for Aza-CMP-Co. Benefiting from the enhanced catalytic kinetics, the Aza-CMP-Co/CP electrode necessitates overpotentials of 324 mV and 370 mV to achieve current densities of 10 mA cm\(^{-2}\) and 100 mA cm\(^{-2}\), respectively. The amount of redox-active Co\(^{2+}\) sites was calculated through the linear relationship between the peak current of Co\(^{2+/3+}\) redox and scan rates (Figure 77a). Aza-CMP-Co/CP displays active cobalt site concentrations of 8.52×10^{-9} mol cm\(^{-2}\), corroborating molecular loading magnitudes commonly observed for porous substrates (Figure 77b). TOFs were calculated based on the redox-active Co\(^{2+}\) sites (TOF\(_{\text{redox-active}}\)) and total Co content (TOF\(_{\text{total-content}}\)). The TOFs logarithm varies linearly as a function of the applied overpotentials between 280 and 360 mV (Figure 76b). Notably, Aza-CMP-Co achieves a TOF\(_{\text{redox-active}}\) rate of 0.95 s\(^{-1}\) at an overpotential of 300 mV, escalating to 10.6 s\(^{-1}\) at 350 mV, outperforming most cobalt oxide/hydroxide-based catalysts in electrocatalytic alkaline water oxidation (Table 5). The durability of the Aza-CMP-Co/CP electrode was verified through chronopotentiometry analysis in 1.0 M NaOH. Following a 5-hour electrolysis test, a constant potential of 1.557 V is required to maintain a current density of 10 mA cm\(^{-2}\), attesting to the operational stability of the catalyst (Figure 76e).

The water oxidation performance of Aza-CMP-Co was further investigated under near-neutral conditions (0.5 M sodium borate buffer, pH 9.2). The Aza-CMP-Co/CP requires overpotentials of 388 and 446 mV to achieve current densities of 1.0 and 10 mA cm\(^{-2}\), respectively (Figure 76e). The calculated Tafel slope is 68.7 mV dec\(^{-1}\), suggesting relatively fast kinetics under these conditions. The amount of active cobalt sites was determined via a Co\(^{2+/3+}\) redox method, resulting in loading levels of 8.46×10^{-9} mol cm\(^{-2}\), which is consistent with those observed in alkaline environments (Figure 77d). The TOF\(_{\text{redox-active}}\) and TOF\(_{\text{total-content}}\) values demonstrate exponential increases with applied overpotentials ranging between 360 mV and 440 mV. Specifically, the TOF rate reaches 1.0 s\(^{-1}\) per redox-active Co\(^{2+}\) site at an applied overpotential of 425 mV and escalates to 2.9 s\(^{-1}\) at 450 mV (Figure 76d). Remarkably, Aza-CMP-Co exhibits superior water oxidation performance compared to most other cobalt-based electrocatalysts under near-neutral conditions (Table 6). Despite the common performance degradation when transitioning from alkaline to near-neutral conditions, the Aza-CMP-Co catalyst sustains a high level of activity, outperforming state-
of-the-art cobalt-based electrocatalysts operating under identical conditions. The durability was confirmed through chronopotentiometry, with the Aza-CMP-Co/CP electrode requiring approximately a potential of 1.72 V to maintain a current density of 10 mA cm$^{-2}$, attesting to its good stability in near-neutral environments (Figure 76f).

Figure 76. (a) LSV curves of Aza-CMP-Co and reference samples in 1.0 M NaOH (scan rate: 1 mV s$^{-1}$). Inset: corresponding Tafel slopes. (b) TOFs of Aza-CMP-Co under various overpotentials in 1.0 M NaOH. (c) LSV curves of Aza-CMP-Co and reference samples in 0.5 M NaBi buffer (pH 9.2, scan rate: 5 mV s$^{-1}$). Inset: corresponding Tafel slopes. (d) TOFs of Aza-CMP-Co under various overpotentials in 0.5 M NaBi buffer. Chronopotentiometry measurement of Aza-CMP-Co at a current density of 10 mA cm$^{-2}$ for 5 hours in (e) 1.0 M NaOH and (f) 0.5 M NaBi buffer.
Figure 77. (a) CV curves of Aza-CMP-Co/CP electrode at different scan rates in 1.0 M NaOH solutions and (b) corresponding dependence of peak current density on scan rates. (c) CV curves of Aza-CMP-Co/CP electrode at different scan rates in 0.5 M NaBi buffer solutions and (d) corresponding dependence of peak current density on scan rates.

Table 5. Water oxidation performance of recently published cobalt-based catalysts under basic conditions.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Overpotential (mV)</th>
<th>Tafel slope (mV dec⁻¹)</th>
<th>TOF (s⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aza-CMP-Co</td>
<td>324 (10 mA cm⁻²)</td>
<td>43</td>
<td>10.6 (350 mV) 0.95 (300 mV)</td>
<td>This work</td>
</tr>
<tr>
<td>CoOOH NS</td>
<td>300 (10 mA cm⁻²)</td>
<td>38</td>
<td>0.09 (340 mV)</td>
<td>460</td>
</tr>
<tr>
<td>PHI-Co</td>
<td>324 (10 mA cm⁻²)</td>
<td>44</td>
<td>1.5 (350 mV)</td>
<td>187</td>
</tr>
<tr>
<td>macro-TpBpy-Co</td>
<td>380 (10 mA cm⁻²)</td>
<td>54</td>
<td>0.089 (400 mV)</td>
<td>461</td>
</tr>
<tr>
<td>TpBpy-Co</td>
<td>430 (10 mA cm⁻²)</td>
<td>58</td>
<td>0.018 (400 mV)</td>
<td>461</td>
</tr>
<tr>
<td>Co-N,S-graphene</td>
<td>370 (10 mA cm⁻²)</td>
<td>62</td>
<td>0.27 (350 mV)</td>
<td>186</td>
</tr>
<tr>
<td>CoOx-ZIF/C</td>
<td>319 (10 mA cm⁻²)</td>
<td>70</td>
<td>0.08 (320 mV)</td>
<td>462</td>
</tr>
<tr>
<td>CUMSs-ZIF-67</td>
<td>320 (10 mA cm⁻²)</td>
<td>53</td>
<td>0.46 (300 mV)</td>
<td>207</td>
</tr>
<tr>
<td>Co-g-C3N4-CNT</td>
<td>370 (10 mA cm⁻²)</td>
<td>62</td>
<td>-</td>
<td>463</td>
</tr>
<tr>
<td>CoN4/NG</td>
<td>380 (10 mA cm⁻²)</td>
<td>81</td>
<td>-</td>
<td>464</td>
</tr>
<tr>
<td>Co-POC</td>
<td>470 (10 mA cm⁻²)</td>
<td>139</td>
<td>-</td>
<td>465</td>
</tr>
<tr>
<td>UNT Co SAs/N-C</td>
<td>380 (10 mA cm⁻²)</td>
<td>70</td>
<td>-</td>
<td>466</td>
</tr>
</tbody>
</table>
Table 6. Water oxidation performance of recently published cobalt-based catalysts under near-neutral conditions.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Overpotential (mV)</th>
<th>Tafel slope (mV dec⁻¹)</th>
<th>TOF (s⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aza-CMP-Co</td>
<td>446 (10 mA cm⁻²)</td>
<td>69</td>
<td>0.37 (400 mV)</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>388 (1 mA cm⁻²)</td>
<td></td>
<td>2.9 (450 mV)</td>
<td></td>
</tr>
<tr>
<td>Co-Pi</td>
<td>410 (1 mA cm⁻²)</td>
<td>60</td>
<td>-</td>
<td>130</td>
</tr>
<tr>
<td>Co₃O₄ QDs</td>
<td>490 (10 mA cm⁻²)</td>
<td>80</td>
<td>0.07 (520 mV)</td>
<td>467</td>
</tr>
<tr>
<td>Co-TpBpy</td>
<td>400 (1 mA cm⁻²)</td>
<td>-</td>
<td>0.23 (400 mV)</td>
<td>220</td>
</tr>
<tr>
<td>Co-based</td>
<td>550 (1 mA cm⁻²)</td>
<td>-</td>
<td>0.017 (530 mV)</td>
<td>433</td>
</tr>
<tr>
<td>Co@CB[5]/ITO</td>
<td>480 (1 mA cm⁻²)</td>
<td>59.5</td>
<td>4.2 (530 mV)</td>
<td>329</td>
</tr>
<tr>
<td>Co-Pi NA/Ti</td>
<td>420 (10 mA cm⁻²)</td>
<td>187</td>
<td>0.037 (410 mV)</td>
<td>468</td>
</tr>
<tr>
<td>Co-Bi/GCE</td>
<td>395 (1 mA cm⁻²)</td>
<td>-</td>
<td>-</td>
<td>469</td>
</tr>
</tbody>
</table>

The electrochemical production of oxygen from the Aza-CMP-Co system was confirmed through a pressure transducer. In 1.0 M NaOH and 0.5 M NaBi solutions, the quantitative yields of Aza-CMP-Co/CP are found to be 98.8% and 98.3%, respectively, signifying that nearly all the accumulated charge through the Aza-CMP-Co electrodes participates in the water oxidation reaction (Figures 78a and 78b). To ascertain that the molecular cobalt sites in Aza-CMP-Co induce the OER activity, an ethylenediaminetetraacetate (EDTA) treatment experiment was performed. The strong chelation ability of EDTA leads to the detachment of cobalt ions from their coordination sites in Aza-CMP-Co. Consequently, the EDTA-treated samples exhibit neither redox characteristics nor OER activity, substantiating that the catalytic water oxidation currents are contributed by the coordinated cobalt sites in Aza-CMP-Co (Figure 78c). Furthermore, LSV studies of Aza-CMP-Co/CP reveal comparable OER current densities under both stationary and rotating conditions, thus attesting to efficient mass transport on the electrode surface during water oxidation, an anticipated feature for 2D porous structures (Figure 78d).
Figure 78. Faradaic efficiencies of Aza-CMP-Co for water oxidation in (a) 1.0 M NaOH and (b) 0.5 M NaBi. Theoretically calculated and experimentally measured amounts of O₂ were shown as functions of electric charge for water splitting catalyzed by Aza-CMP-Co at a current density of 20 mA cm⁻². The quantitative yields of Aza-CMP-Co equal 98.8% in 1.0 M NaOH and 98.3% in 0.5 M NaBi. (c) CVs of Aza-CMP-Co/CP before and after being treated with 0.1 M EDTA/0.01 M NaOH aqueous solution (1.0 M NaOH, 50 mV s⁻¹ scan rate, without iR compensation). (d) The LSV measurements of Aza-CMP-Co/CP under stationary and rotating conditions (1.0 M NaOH, 50 mV s⁻¹ scan rate).

Notably, Aza-CMP-Co maintains its redox characteristics and catalytic current density even after 400 CV scans in diverse electrolytes, highlighting the stability of single-site cobalt toward OER under broad pH conditions (Figure 79d). XANES and EXAFS spectra in R- and k-spaces were plotted to further illustrate the alterations in coordination environments following oxygen evolution. The nearly superimposable curves in Figures 79a-c indicate negligible modifications in the first-coordination sphere surrounding the cobalt active sites post-OER.
Electrocatalytic water oxidation under mild pH conditions typically exhibits low catalytic activity and high overpotentials. Despite its satisfactory performance in near-neutral conditions relative to other known systems, the Aza-CMP-Co catalyst experiences considerable degradation in key performance metrics, including overpotential, onset potential, Tafel slopes, and TOFs, upon transitioning from an alkaline to a mildly basic electrolyte. The structurally well-defined Aza-CMP-Co catalyst, featuring Co^{2+} active sites within a uniform CMP framework, serves as an exemplary platform for in-depth mechanistic investigations upon such puzzles.

The pH-dependent performance studies were first conducted in NaOH solutions to investigate the proton-electron transfer process at cobalt sites in alkaline conditions ([Figure 80a](#figure80a)). The Pourbaix diagram reveals a slope of \(-117 \text{ mV pH}^{-1}\) for the Co^{2+/3+} redox couple, indicative of a two-proton, one-electron transfer process (\(2\text{H}^+/1\text{e}^-\)); for the Co^{3+/4+} redox pair, a slope of \(-63 \text{ mV pH}^{-1}\) corresponds to a 1H^+/1e^- transfer process ([Figure 80b](#figure80b)).
Remarkably, these PCET characteristics align with the reported molecular cobalt-based heterogeneous electrocatalyst.\textsuperscript{186}

**Figure 80.** (a) CV and DPV curves of Aza-CMP-Co in different pH conditions (unbuffered NaOH solutions) and (b) corresponding Pourbaix diagram (scan rate: 50 mV s\(^{-1}\), without iR compensation. \(L = \text{OH or H}_2\text{O ligand according to the Co}^{-N_2/O_4}\) moiety that was determined by EXAFS analysis). (c) pH-dependent OER activity (potential determined at 2.0 mA cm\(^{-2}\)). (d) LSV curves of the Aza-CMP-Co in 1.0 M NaOD/D\(_2\)O and NaOH/H\(_2\)O solutions (scan rate: 5 mV s\(^{-1}\)), inset: KIEs against potential. (e) CV curves of Aza-CMP-Co under different pH conditions (borate buffered solutions) and (f) corresponding Pourbaix diagram (scan rate: 50 mV s\(^{-1}\), without iR compensation). (g) pH-dependent OER activity (potential determined at 2.0 mA cm\(^{-2}\) in NaBi buffer). (h) LSV curves of Aza-CMP-Co in 0.1 M NaBi/D\(_2\)O and NaBi/H\(_2\)O solutions (scan rate: 5 mV s\(^{-1}\)), inset: KIEs against overpotential.
Subsequent pH-dependent studies were conducted under near-neutral conditions using a borate buffer (Figure 80e). As shown in Figure 80f, the initial Co$^{2+/3+}$ redox process discernible between pH 6 and 9 pertains to the oxidation of [N$_2$L$_2$Co$^2+$(OH$_2$)$_2$] to [N$_2$L$_2$Co$^3+$(OH$_2$)(OH)], accompanied by the loss of a single proton (where L denotes either OH$^-$ or H$_2$O ligand and N represents a coordinated nitrogen atom from Aza-CMP). A clear inflection point appears in the Co$^{2+/3+}$ curve at pH levels exceeding 9, and a two-proton transfer process is inferred based on a slope value of $-115$ mV pH$^{-1}$. The p$K_a$ value of [N$_2$L$_2$Co$^3+$(OH$_2$)(OH)] is thus approximated to be near 9. In addition, the PCET properties of Co$^{3+/4+}$ maintain its 1H$^+/1e^-$ feature across a broad pH range of 6 to 13, suggesting that the cobalt sites undergo a consistent Co$^{3+/4+}$ pathway, thereby emphasizing the significance of pH in accessing reactive species. Notably, these redox behaviors closely parallel those of Ru$^{2+/3+}$ and Ru$^{3+/4+}$ in cis-[(bpy)$_2$Ru$^{II}$(OH$_2$)$_2$]$^{2+}$, where the inflection point is identified at pH 5.5.$^{470}$

The KIE$_{H/D}$ for Aza-CMP-Co were assessed to validate the proton transfer mechanism within the RDS of the catalysis. The LSV curve of Aza-CMP-Co/CP in a 1.0 M NaOD D$_2$O solution reveals a slightly reduced current density compared to that in a 1.0 M NaOH aqueous solution (Figure 80d). Correspondingly, The KIE$_{H/D}$ values are found to be less than 1.5 across the overpotential range of 0.3-0.36 V. In alignment with the LSV-derived data, KIEs measured via chronoamperometry approximate 1.4 within the overpotential scope of 0.32 to 0.36 V in alkaline conditions, thereby suggesting a secondary KIE where O-H bond cleavage may not be directly involved in the RDS. Conversely, under near-neutral conditions in a borate buffer, KIE$_{H/D}$ values exceeding 1.8 are observed within the catalytic overpotential range, indicating a primary KIE effect (Figure 80h). This absence of a primary KIE in Aza-CMP-Co corroborates that, under alkaline conditions, (i) O-H bond cleavage is not involved in the RDS, and (ii) the decoupled ET process likely constitutes the RDS of OER.

The pH-dependent OER activity can serve as an indicator of the proton-electron transfer characteristics inherent to RDS. Potential shifts at the catalytic current density of 2.0 mA cm$^{-2}$ were analyzed for Aza-CMP-Co to evaluate the pH-dependency of activity. In alkaline conditions, linear fitting reveals that the NHE potentials associated with the OER catalytic waves shifted concomitant with pH changes, exhibiting slopes approximating $-59$ mV pH$^{-1}$ (i.e., zero-order dependency on OH$^-$ concentration at the RHE scale) (Figure 80c). Although such zero-order dependency typically indicates a CPET process in the RDS, the secondary KIEs observed for Aza-CMP-Co contradict this interpretation. Two alternative explanations arise: firstly, the
pH-independent OER activities of the ET-controlled catalytic event at the RHE scale could result from a pre-RDS (1H+/1e− in this case) constrained pH dependence; secondly, the OER catalyzed by Aza-CMP-Co may typify a heterogeneous catalytic reaction, wherein the rate depends on active site abundance and driving forces, rather than on reactant concentration.471 Regardless, the absence of primary KIEs in alkaline conditions strongly suggests a non-concerted proton-electron transfer in the RDS of Aza-CMP-Co, whereas under near-neutral conditions, pH-independent activities at the RHE scale (Figure 80g), and primary KIEs are consistent with a concerted APT mechanism.

4.4 Non-aqueous redox and quantitative CV analysis

To investigate the involvement of successive redox processes after the Co4+ state, CV experiments were conducted in an acetonitrile-based non-aqueous electrolyte, where the substrate concentration (H2O, HO−) is significantly minimized. These conditions effectively suppress OER, enabling the electrochemical identification of higher-valent reactive intermediates.151 As evidenced in Figure 81a, the CV curve of the Aza-CMP-Co/CP electrode under anhydrous conditions presents several oxidation peaks. The electrochemical potentials corresponding to these oxidations were quantitatively evaluated by DPV (Figure 81c). Oxidation peaks at potentials of 0.13 V and 0.47 V are ascribed to the sequential oxidations from Co2+ to Co3+ and Co3+ to Co4+, respectively. Peaks at 0.67 V and 0.88 V, previously undetected in aqueous environments, are likely linked to successive PCET processes. Upon introduction of water and NaOH into the electrolyte, a noticeable catalytic current was observed (Figure 81b). The third and fourth redox peaks, which correspond to successive redox processes, become subsumed within this catalytic current during OER. Given the secondary KIEs, one of the additional redox features could potentially be linked to the electron transfer process of the RDS under alkaline conditions.

The experimental CV data of Aza-CMP-Co was compared with the theoretically expected CV behavior generated from an irreversible monolayer adsorption model (see supporting information of Paper II for detailed derivations). As shown in Figure 81d, the observed CV behavior of Aza-CMP-Co aligns well quantitatively with the predictions of the model. For the reversible Co2+/3+ redox couple, the calculated current-potential data points exhibit excellent agreement with the experimental curve. These results suggest that Aza-CMP-Co operates as adsorbed cobalt monolayers with a loading density of 8.5 × 10−9 mol cm−2, displaying nearly ideal Nernstian behavior. This provides further evidence for the molecular nature of Aza-CMP-Co. The Co3+/4+ oxidation occurs via an irreversible, one-electron, one-
step process. For OER current calculation in the foot of the wave area, the irreversible Co\(^{4+}\) oxidation reaction is assumed as the RDS for OER, and the formal potential of Co\(^{4+}\) oxidation is estimated by DPV under non-aqueous conditions in Figure 81c, but with intrinsic limitations. Figure 81d reveals that the calculated forward and backward scan catalytic currents match well with the experimental CV, with an apparent rate constant \((k_{ap})\) of around 18.5 s\(^{-1}\). This comprehensive electrochemical evaluation corroborates the molecular nature of the as-fabricated Aza-CMP-Co, as predicted by the irreversible monolayer adsorption model. Given its precision, the quantitative CV analysis should be prioritized as a tool to ascertain the uniformity and molecular features of the catalytic center, especially for single-atom catalysts, before proceeding with detailed mechanistic studies.

![Figure 81](image)

**Figure 81.** (a) CV curves of Aza-CMP-Co and Aza-CMP on carbon paper in dry acetonitrile (scan rate: 50 mV s\(^{-1}\)). (b) CV curves of Aza-CMP-Co when adding water and NaOH to the non-aqueous electrolyte. (c) DPV curves of Aza-CMP-Co in acetonitrile and water/NaOH added acetonitrile electrolytes. (d) Calculated CV curve for Aza-CMP-Co (1.0 M NaOH, scan rate: 50 mV s\(^{-1}\)).

### 4.5 APT mechanism clarification

When the rate-limiting O-O bond formation involves APT within the water nucleophilic attack pathway, the introduction of external anions (e.g., phosphate, acetate, or borate) as proton acceptors significantly accelerate the rate of water oxidation.\(^{345, 472, 473}\) Typically, the first-order reactions with respect to these anions are commonly observed when the RDS of OER proceeds via a diffusion-controlled solution APT mechanism (Figure 82).\(^{214}\)
In addition to the influence of the base, the impact of cations in the solution should not be overlooked. The cation effect in the oxygen evolution is associated with the interaction of the cation with active oxygenated species,\textsuperscript{167, 477-479} enabling the differentiation between the intermolecular diffusion-controlled solution APT process and the intramolecular oxyl/oxo coupling process.

\textbf{Figure 82. Schematic diagram of the possible “anion” and “cation” effects for the O-O bond formation process.}

For elucidating the OER mechanism through kinetic studies, cobalt hydroxide (Co(OH)\textsubscript{2}) was chosen as an example material to verify the methodology. As shown in Figure 83a, cobalt hydroxide and Aza-CMP-Co exhibit distinct redox features, suggesting the presence of divergent redox species in the two systems. As illustrated in the Pourbaix diagram, the Co\textsuperscript{2+/3+} redox couple of Co(OH)\textsubscript{2} exhibits a slope of –84 mV pH\textsuperscript{−1}, signifying a three-proton, two-electron transfer process (3H\textsuperscript{+}/2e\textsuperscript{−}) or a composite proton-transfer mechanism (Figure 83c). For the Co\textsuperscript{3+/4+} redox couple, the slope is measured at –61 mV per pH, which is indicative of a 1H\textsuperscript{+}/1e\textsuperscript{−} transfer process. Under alkaline conditions, a slope value of –60 mV pH\textsuperscript{−1} suggests that cobalt hydroxide demonstrates no pH-dependent OER activity on the RHE scale (Figure 83e). The associated KIE\textsubscript{H/D} values are approximately 2.4 across the catalytic overpotential range, thereby denoting primary KIEs and implying a concerted APT process during the RDS (Figure 83d).

As previously stated, incorporating a Lewis base as a proton acceptor can markedly enhance the kinetics of the APT reaction. Consequently, the role of mediating APT in cobalt hydroxide-catalyzed water oxidation was
investigated by introducing varying concentrations of phosphate in an alkaline pH environment. The reaction order based on phosphate \( \rho_{[\text{phosphate}]} \) for the cobalt hydroxide is calculated to be approximately 0.4 under pH 12.6 conditions, which indicates that the RDS of cobalt hydroxide catalyzed water oxidation follows a concerted solution APT with O-atom of a water molecule transfer to the M=O coupled with a proton transfer to the base acceptor(s) in solution (Figure 84a). In contrast, Aza-CMP-Co exhibits a zero-order dependence on \( \rho_{[\text{phosphate}]} \) under identical conditions, suggesting a fundamentally distinct RDS (Figure 84b). The impact of cations on cobalt hydroxide was investigated using LSV in a 1.0 M MOH solution, where M represents Li, Na, and K (Figure 84c). A decline in OER activity is observed when transitioning from K\(^+\) to Li\(^+\) cations, highlighting the substantial role of hydrogen-bonded networks and solvation strength in the solution APT process. For Aza-CMP-Co catalyzed OER, no such cation dependencies are observed under alkaline conditions (Figure 84d). The aforementioned experiments reveal two key insights: 1) the interplay of pH-dependency, KIEs, and anion/cation effects effectively characterize the APT process; 2) under alkaline conditions, Aza-CMP-Co exhibits different RDS and key intermediates compared to cobalt hydroxide, underscoring the distinctiveness of molecular systems.

Figure 83. (a) CV curves of Aza-CMP-Co and cobalt(II) hydroxide recorded in 1.0 M NaOH. (b) CV curves of cobalt(II) hydroxide recorded at different pH (NaOH solutions) and (c) the corresponding Pourbaix diagram (scan rate = 50 mV s\(^{-1}\), no iR compensation). (d) LSV curves of cobalt(II) hydroxide recorded in 1.0 M NaOD/D\(_2\)O and NaOH/H\(_2\)O (scan rate = 5 mV s\(^{-1}\)), inset: KIEs-overpotential plot. (e) pH-dependent OER activity (potential at 1.0 mA cm\(^{-2}\)).
4.6 pH-related nucleophilic attack

To further understand the role of mediated APT in cobalt-site-catalyzed water oxidation, the anion concentration-activity dependency of Aza-CMP-Co was examined across different pH. A significant anion effect is observed at pH 7.7, but not at pH 11.0 and 13.3 (Figures 85b-d). At pH 7.7, the rate parameter $\rho_{[\text{borate}]}$ for the cobalt sites ranges approximately from 0.5 to 0.7 across the entire catalytic potential scale. Given the moderate KIE$_{\text{H/D}}$ value of around 1.8 in near-neutral conditions and the presence of adjacent, uncoordinated nitrogen sites in Aza-CMP, the APT process in solution occurs in tandem with a second coordination sphere-assisted proton transfer at the cobalt sites. In contrast, at pH 11.0 and 13.3, $\rho_{[\text{borate}]}$ values approach zero, suggesting a negligible role for anions in the RDS and excluding a solution-based APT process under alkaline conditions.

Figure 84. LSV curves of (a) cobalt(II) hydroxide and (b) Aza-CMP-Co recorded at different [Pi] under pH 12.6. Inset: corresponding reaction order with respect to Pi (scan rate: 5 mV s$^{-1}$). LSV curves of (c) cobalt(II) hydroxide and (d) Aza-CMP-Co recorded in 1.0 M KOH, NaOH, and LiOH. Inset: comparison of catalytic currents at different potentials (scan rate: 50 mV s$^{-1}$).
Figure 85. (a) Comparison of kinetic phenomena and effects under different conditions. LSV curves of Aza-CMP-Co as a function of [NaBi] at (b) pH 7.7, (c) pH 13.3, and (d) pH 11.0 (scan rate: 5 mV s$^{-1}$). Inset: corresponding reaction order of [Bi]. (e) LSV curves of Aza-CMP-Co in 1.0 M KOH, NaOH, and LiOH (scan rate: 5 mV s$^{-1}$). Inset: comparison of catalytic currents at different potentials. (f) LSV curves of Aza-CMP-Co in 0.5 M KBi, NaBi, and LiBi (scan rate: 5 mV s$^{-1}$). Inset: comparison of catalytic currents at different potentials.

The electrocatalytic behavior of Aza-CMP-Co was further assessed using LSV in 1.0 M MOH solutions (where M represents Li, Na, or K) as well as in 0.5 M MBi solutions. As shown in Figure 85f, when the OER occurs in borate buffers, a decline in activity is observed when transitioning from K$^+$ to Li$^+$ cations. This suggests that the hydrogen bonding network and solvation strength substantially impact the solution-based APT process. In contrast,
**Figure 85e** reveals that the nature of the cationic species does not influence the catalytic performance of Aza-CMP-Co under alkaline conditions.

**Figure 85a** lists the kinetic characteristics of Aza-CMP-Co in both near-neutral and alkaline conditions. Notably, distinct variations in catalytic kinetics emerge when varying the pH. In near-neutral conditions, the water oxidation activity of Aza-CMP-Co is notably influenced by anion concentration and cationic species, signifying that the RDS is governed by a solution-based APT process. Under alkaline conditions, Co(OH)\textsubscript{2}, employed as a reference material, also conforms closely to the anticipated behavior of a solution-based APT process. However, the OER catalyzed by Aza-CMP-Co deviates significantly from this model: no such dependencies are discernible, implying that the RDS is unaffected by external proton acceptors or varying solvation strength. The absence of KIEs for Aza-CMP-Co in alkaline media indicates that direct O-H bond cleavage is not a component of the RDS. Consequently, elevated anion concentrations do not facilitate OER, as proton transfer is irrelevant to the RDS. If the source of the oxygen atom for O-O bond formation is not directly from inner Helmholtz plane H\textsubscript{2}O/OH\textsuperscript{−} molecules; it likely originates from adjacent pre-deprotonated H\textsubscript{2}O molecules, i.e., the OH ligands generated by the decoupled 2H\textsuperscript{+}/1e\textsuperscript{−} Co\textsuperscript{2+/3+} redox. Therefore, the absence of dependency on solvation strength in alkaline conditions is ascribed to the intramolecular hydroxyl transfer process controlling the RDS (**Figure 82**).

### 4.7 Reaction activation energy analysis

The activation energy is intrinsically linked to the specific reaction pathway for a given catalyst. Hence, to obtain insights into the intrinsic OER activity and to discern the mechanism variations of cobalt sites under alkaline and near-neutral conditions, activation energy was assessed in both NaOH and NaBi buffer solutions employing temperature-regulated electrocatalysis. **Figures 86a** and **86b** reveal a distinct temperature-dependent feature in the OER activity of Aza-CMP-Co under both solution environments. Activation energy \( W \) was plotted against the overpotential, displaying a linear relationship as illustrated in **Figure 86c**. Notably, \( W \) under alkaline conditions (\( W_{\text{alkaline}} \)) is markedly lower than under near-neutral conditions (\( W_{\text{neutral}} \)). Within the OER catalytic overpotential range of 0.3 to 0.5 V, the difference (\( \Delta W \)) evolves linearly from 4.45 to 0.96 kcal mol\textsuperscript{−1}, indicative of a TOF gap ranging from \( 10^3 \) to \( 10^1 \) times at different overpotentials. Given that the activation energy is independent of external variables, such differences in \( W \) point to divergent RDS intermediates, leading to marked variances in the inherent catalytic performance.
**Figure 86.** (a) Temperature-dependent LSV curves of Aza-CMP-Co catalyzed OER at different overpotentials in (a) 1.0 M NaOH and (b) pH 9 NaBi buffer (scan rate: 5 mV s$^{-1}$). (c) Plots of overpotential-dependent activation energy against reaction overpotential. (d) Calculated energy profiles of WNA (blue) and IHNA (red) pathways. (e) Chemical structure of O-O formation intermediates in WNA and IHNA pathways. Relative solvation-corrected electronic energies are given in eV and O-O distances at transition states in Å.

DFT calculations were conducted to elucidate the electrocatalytic water oxidation mechanism. The O-O bond formation from the intermediate [Co$^{IV}$=O(OH)(OH$_2$)$_2$]$^{+}$ (3, **Figure 86d**) was evaluated through the WNA pathway under neutral conditions. This endergonic process necessitates a reaction energy of 8.2 kcal mol$^{-1}$ and an activation energy of 24.6 kcal mol$^{-1}$ (**transition state 1, TS-1, Figure 86e**). Conversely, O-O bond formation through the IHNA pathway, originating from [Co$^{IV}$=O(OH)$_2$(OH$_2$)]$^{+}$ (5, **Figure 86d**), is energetically favored under alkaline conditions relative to the WNA pathway. The associated transition state (**transition state 2, TS-2,**
Figure 86e) reveals reaction and activation energies of $-1.8$ and $21.5$ kcal mol$^{-1}$, respectively. The computed activation energy disparity between the two pathways is $3.1$ kcal mol$^{-1}$, aligning well with the experimentally observed $\Delta W$ values within an overpotential range of $0.32$ V ($4.1$ kcal mol$^{-1}$) to $0.45$ V ($2.1$ kcal mol$^{-1}$). Relative to neutral conditions, the cobalt sites under alkaline conditions exhibit reduced activation energies, unique pH-dependent redox features, smaller KIEs, negligible reaction order with respect to the external anion, and absence of cation effects. Collectively, these findings suggest that the key to understanding the observed OER performance discrepancy between alkaline and near-neutral conditions lies in the $pK_a$-induced, pH-related nucleophilic attack pathway.

4.8 Integrating Aza-CMP-Co with BiVO$_4$ photoanode

The Aza-CMP-Co complex was applied to a BiVO$_4$ electrode via simple drop-casting to evaluate its potential utility in PEC systems. Subsequent PEC performance assessments were conducted on the resulting BiVO$_4$/Aza-CMP-Co photoanode using a borate buffer solution with a pH of $9.3$. As shown in Figure 87a, the incorporation of Aza-CMP-Co significantly enhances the photocurrent density of the BiVO$_4$ photoanode from an initial $1.7$ mA cm$^{-2}$ to $4.3$ mA cm$^{-2}$ at a potential of $1.23$ V vs. RHE. Moreover, the onset photocurrent potential for BiVO$_4$/Aza-CMP-Co shifts negatively, reaching approximately $0.2$ V vs. RHE. According to the obtained LSV data, the ABPE for the BiVO$_4$/Aza-CMP-Co is determined to be approximately $1.62\%$ at $0.6$ V vs. RHE, representing a six-fold improvement over the $0.27\%$ observed for the pristine BiVO$_4$ at $0.9$ V vs. RHE (Figure 87b). The passivation properties of Aza-CMP-Co were examined using IMPS. IMPS plots in Figures 87c and 87d illustrate typical profiles for both bare BiVO$_4$ and BiVO$_4$/Aza-CMP-Co in the complex plane. Extracted $k_{\text{rec}}$ and $k_{\text{trans}}$ are presented in Figures 87e and 87f, in which a marked reduction in $k_{\text{rec}}$ is noted across all potentials for the BiVO$_4$/Aza-CMP-Co electrode. Specifically, at $0.6$ V vs. RHE, the $k_{\text{rec}}$ for BiVO$_4$/Aza-CMP-Co is a mere $0.65$ s$^{-1}$, a value over 20 times lower than bare BiVO$_4$ ($15.2$ s$^{-1}$). This data strongly supports that Aza-CMP-Co significantly passivates surface recombination on the surface of BiVO$_4$. Figure 87e reveals that $k_{\text{trans}}$ for BiVO$_4$/Aza-CMP-Co exceeded that of bare BiVO$_4$ at every applied bias, leading to a superior charge transfer efficiency. Figure 88 schematically summarizes the overall effects of Aza-CMP-Co on both charge transfer and surface recombination in BiVO$_4$. Collectively, these findings highlight that the suppression of surface recombination is a crucial factor contributing to the enhanced PEC performance observed in the BiVO$_4$/Aza-CMP-Co system.
Figure 87. (a) J-V curves of BiVO$_4$ and BiVO$_4$/Aza-CMP-Co photoanodes under AM 1.5G illumination in a borate buffer (pH 9.3). (b) ABPEs of photoanodes. IMPS plots of (c) BiVO$_4$ and (d) BiVO$_4$/Aza-CMP-Co photoanodes at different applied biases. The rate constants of (e) $k_{rec}$ and (f) $k_{trans}$ were extracted from IMPS spectra.
4.9 Conclusions

In summary, the synthesized Aza-CMP-Co exhibits remarkable catalytic efficiency under both neutral and alkaline environments, surpassing the TOFs achieved by state-of-the-art material-based catalysts. Comprehensive experimental and theoretical investigations employing this well-characterized model catalyst reveal that water oxidation catalyzed by the single cobalt triggered a pH-controlled nucleophilic attack pathway. As shown in Figure 89, deprotonation occurs during the oxidation of Co$^{2+}$ to Co$^{3+}$, and two protons detach when the pH is increased above the pK$_a$ value of the Co$^{3+}$ intermediate. The Co$^{4+}$=O fragment is formed when Co$^{3+}$ is further oxidized to Co$^{4+}$ under both near-neutral and alkaline conditions. In the buffered medium, the rate-determining step, specifically step 3, proceeds through a concerted solution APT mechanism that yields a Co-OOH fragment. This mechanism results in normal KIEs H/D and pH-independent OER activity on the RHE scale. However, at elevated pH, the O-O bond formation mechanism diverges considerably. Specifically, the extra -OH group arising from the non-concerted PCET process of Co$^{2+}$/Co$^{3+}$ in alkaline electrolytes tends to facilitate Co-OOH fragment formation via an intramolecular hydroxyl nucleophilic attack pathway, where the adjacent hydroxyl group attacks the oxo ligand in Co$^{4+}$=O, leading to an intramolecular O-O bond. This mechanism results in a secondary KIEs H/D and cation/anion-independent OER activity. Ultimately, the -OOH ligand undergoes a subsequent 1H$^+$/1e$^-$ PCET process, converting to dioxygen, allowing for substrate reattachment, and thus completing the catalytic cycle. The IHNA pathway necessitates substantially lower activation energy than its intermolecular WNA counterpart, thereby elucidating the significant performance loss when
transitioning from an alkaline to a near-neutral electrolyte. Moreover, the proposed facile fabrication strategy for heterogeneous molecular electrocatalysts and the series of comprehensive OER kinetic studies are amenable to extension across a diverse range of transition metal species, unlocking opportunities for research in heterogeneous molecular (photo)electrocatalytic systems.

Figure 89. Proposed OER mechanisms, including (a) WNA and (b) IHNA; under the basic pH range, the non-concerted PCET process in Co$^{2+/3+}$ redox facilitates the IHNA pathway.
5. Monolithic FAPbBr₃ Photoanode for Photoelectrochemical Water Oxidation

(Paper III, Copyright 2023, Springer Nature)

**Figure 90.** Schematic illustration of FAPbBr₃ photoanode for photo-driven water oxidation.

Despite significant advancements in PEC water splitting research over the past several decades, the transition to practical applications remains constrained by the lack of efficient, stable, and scalable photoelectrodes. Although materials that absorb visible light, such as WO₃, BiVO₄, and Fe₂O₃, have garnered extensive attention due to their favorable band edge positions, the limited charge separation and transport properties continue to hinder their commercial viability. Even single-junction semiconductor photoelectrodes fabricated from wide band gap materials like TiO₂ and WO₃ suffer from high current onset potentials due to high thermodynamic requirements and the complex multi-proton and electron transfer processes intrinsic to water oxidation reactions. Thus, the development of a “perfect” semiconductor characterized by stability, cost-effectiveness, optimal band structures, enhanced charge carrier mobility, and broad absorption remains a considerable challenge. Concurrently, there is a pressing need for more efficient WOCs along with robust, stable, and cost-effective catalyst loading techniques to engineer high-performance water oxidation photoanodes.

Alternatively, PV materials, such as Si, GaAs, and GaInP, known for their superior optical and electronic properties, can serve as absorber layers in integrated solar hydrogen devices, analogous to the semiconductor layers in
conventional PEC configurations. Among various PV absorbers, lead halide perovskites stand out as promising replacements for traditional metal-oxide-based photoelectrodes, owing to their exceptional optoelectronic properties and low-cost, solution-based fabrications. These perovskite materials offer several advantages, including enhanced light absorption coefficients, facile exciton dissociation ability, and extended carrier diffusion lengths. Additionally, the adaptability of their unique crystal structure allows for facile electronic property tuning through compositional variations, making them an attractive platform for high-performance PEC systems. Upon a comprehensive evaluation of factors, such as preparation difficulty, band structure, and material stability, formamidinium lead bromide (FAPbBr₃) was selected as the optimal candidate for developing efficient and stable photoanodes. In this chapter, the FAPbBr₃ absorber layer was employed to build the first monolithic FAPbBr₃-based photoanode for solar water oxidation (Figure 90). The structure-optimized photoanode, featuring integrated carbon/graphite/alloy interlayers and electrodeposited NiFe LDH catalyst, exhibits superior performance and stability, surpassing the most advanced single-junction absorber photoanodes reported to date. This research serves as a pivotal guide for advancing photovoltaic material-based photoelectrodes in solar fuel technologies.

5.1 Photoanode preparation and characterizations

The FAPbBr₃ perovskite photoanode comprises two parts: the light-absorbing part (ITO/SnO₂/FAPbBr₃/carbon) and the WOC part (graphite sheet/NiFe alloy/NiFe LDH); to prevent water-induced degradation of the FAPbBr₃ material, the edge of the device is sealed with commercially available epoxy resin. The light-absorbing part, which is a hole transport material (HTM)-free FAPbBr₃ solar cell, is schematically shown in Figure 91a. In the as-fabricated FAPbBr₃/carbon solar cell, the FAPbBr₃ layer, with a thickness of around 400 nm, is sandwiched between a compact SnO₂ layer and a conductive mesoporous carbon layer (Figure 91b). The champion device shows a PCE of 9.2% with a high $V_{oc}$ of 1.38 V, a $J_{sc}$ of 8.69 mA cm$^{-2}$, and an FF of 76.04% (Figure 91c); the performance is even superior to the reference device using Spiro-MeOTAD as HTM, demonstrating the promising potential for fabricating a low onset potential photoanode using a simple HTM-free configuration. The device shows a high IPCE of over 70% from wavelengths 350 to 550 nm, leading to an integral current density near 7.4 mA cm$^{-2}$ (Figure 91d). The gap between the measured $J_{sc}$ and integrated $J_{sc}$ was also reported in other FAPbBr₃ solar cells and may be caused by different illumination intensities for the IPCE measurements compared to the $J-V$ measurements.
Figure 91. (a) Device structure of HTM-free FAPbBr$_3$/Carbon solar cell. (b) SEM image of HTM-free FAPbBr$_3$/Carbon solar cell in cross-section view. (c) Representative J-V curves of FAPbBr$_3$/Carbon solar cell and reference solar cells. (d) IPCE spectrum of FAPbBr$_3$/Carbon solar cell. Stability tests of FAPbBr$_3$/Carbon solar cell under (e) dry-air conditions and (f) one-sun conditions.

With the protection of the hydrophobic carbon layer, the FAPbBr$_3$/Carbon device retains 106% of its initial efficiency under dry-air conditions over a 300-day period (Figure 91e). When assessed for photostability under continuous one-sun illumination (in open-circuit conditions), the device demonstrates no performance degradation after 72 hours and maintains 73% of its original efficiency following 160 hours of exposure (Figure 91f). The high voltage, outstanding stability, and hydrophobic characteristics of HTM-
free FAPbBr₃/Carbon devices offer distinct advantages for constructing FAPbBr₃-based PEC water oxidation systems.

A 160 μm commercially available self-adhesive GS was positioned atop the FAPbBr₃/carbon layer to prevent water penetration into the light-absorbing part. This compact, stacked GS layer not only affords exceptional thermal (350 W m⁻¹ K⁻¹) and electrical conductivities but also enhances the resistance of the perovskite layer to water permeation. Moreover, its self-adhesive and readily available nature simplifies the device assembly process, rendering it an optimal water separator component for perovskite photoanode construction. Through straightforward electrodeposition techniques, material WOCs can be conveniently attached to the conductive GS layer, thereby allowing independent optimization of the WOC component on the ITO/GS substrate. In our system, a compact attached NiFe alloy layer was first electrodeposited on the GS substrate to improve the adhesion of the hydroxide-based catalyst. Then, active NiFe LDH was electrodeposited onto the GS/NiFe alloy to create a stable and highly active GS/NiFe alloy/NiFe LDH part (Figure 92a). Figure 92b demonstrates that the GS/NiFe alloy/NiFe LDH electrode exhibits the highest catalytic activity compared to the reference GS/NiFe alloy and GS/NiFe LDH electrodes in 1.0 M KOH. The overpotential requirement is significantly reduced in the composite GS/NiFe alloy/NiFe LDH electrode, with only 228 mV required to reach a current density of 10 mA cm⁻², which is 61 and 69 mV lower than that of the GS/NiFe LDH and GS/NiFe alloy electrodes, respectively. Figure 92c presents the corresponding Tafel slopes derived from LSV curves, which are around 30 to 40 mV dec⁻¹, suggesting the presence of similar active NiFe species on the surface of all the electrodes. The inset within Figure 92b shows the zoomed LSV curves corresponding to the Ni²⁺/³⁺ redox region. It reveals that the charge of oxidation peak observed in the GS/NiFe alloy/NiFe LDH electrode substantially surpasses those of the GS/NiFe LDH and GS/NiFe alloy electrodes. Consequently, the amplified current density in the GS/NiFe alloy/NiFe LDH electrode is ascribed to an elevated concentration of the active species. The amount of oxygen electrochemically generated from the GS/NiFe alloy/ NiFe LDH was confirmed using a pressure transducer. Faradic efficiency of 99.3% under 10 mA cm⁻² indicates that accumulated charge is nearly quantitatively consumed in OER (Figure 92d). The catalytic stability was evaluated by chronopotentiometry under a constant current density of 10 mA cm⁻². As shown in Figure 92e, the GS/NiFe alloy/ NiFe LDH electrode exhibits the best stability with only a 19 mV increase in overpotential after 100 hours of catalysis, while the overpotential for the GS/NiFe LDH electrode increased by 81 mV.
5.2 Photoelectrochemical performance of photoanode

Following comprehensive evaluations of the performance and stability of the WOC part, highly active GS/NiFe alloy/NiFe LDH layers were integrated
into the light-absorbing part to construct a photoanode consisting of ITO/SnO2/FAPbBr3/carbon/GS/NiFe alloy/NiFe LDH (i.e., FAPbBr3 photoanode). The images of the FAPbBr3 photoanode are illustrated in Figure 93a. Figure 93b illustrates the LSV curve for the as-fabricated FAPbBr3 photoanode; the photocurrent sharply escalates from –0.12 V vs. RHE and reaches a saturated photocurrent density exceeding 8.5 mA cm\(^{-2}\) at 1.23 V vs. RHE. Statistical analyses of 20 devices reveal an average onset potential of –0.066 V vs. RHE and an average photocurrent density of approximately 8.7 mA cm\(^{-2}\) at 1.23 V vs. RHE. When exposed to chopped-light illumination, the photoanode demonstrates significant current spikes around onset potentials, which indicates slow water oxidation kinetics-induced carrier recombination on the surface (Figure 93c). The accumulated charges may be dissipated through radiative recombination, a process that could damage the perovskite layer and adversely affect the lifetime of the device. The spikes diminish when the potential surpasses 0.2 V vs. RHE, suggesting that only a modest additional driving force is required for the FAPbBr3 photoanode to enhance both the charge separation and the catalytic efficiency. Consequently, this reduces the onset potential prerequisites for counter photocathodes in Z-scheme PEC cells, making it a perfect match with photocathodes, such as CuO or GaInP\(_2\), which have a saturation current of around 10 mA cm\(^{-2}\). IPCEs for the FAPbBr3 photoanode, shown in Figure 93d, were determined under different potentials, revealing approximate IPCE values of 80% and 90% at 0.23 V and 1.23 V vs. RHE, respectively. Upon integrating these IPCE curves over the AM 1.5G solar spectrum, theoretical photocurrent densities are projected to be 7.4 mA cm\(^{-2}\) and 8.3 mA cm\(^{-2}\) at 0.23 V and 1.23 V vs. RHE, respectively, which are consistent with the measured data in Figure 93b. The amount of photogenerated oxygen in the headspace was accurately measured using a pressure transducer. The counts of charges passing the electrode closely correlate with the observed oxygen levels, yielding a Faradaic efficiency of 96.2% at a potential of 1.23 V vs. RHE (Figure 94).
Figure 93. (a) Device structure of FAPbBr$_3$ photoanode. Inset: digital images of as-prepared photoanode. (b) LSV curve of FAPbBr$_3$ photoanode in 1.0 M KOH (scan rate: 50 mV s$^{-1}$). Inset: statistical photoelectrochemical parameters (20 devices) of the onset potential and saturated catalytic current density at 1.23 V vs. RHE. (c) LSV curve of FAPbBr$_3$ photoanode under chopped irradiation (red curve) and density-voltage response of FAPbBr$_3$ photoanode obtained under steady-state current conditions (blue dots) in 1.0 M KOH. (d) IPCEs and corresponding integral current density (AM 1.5G) of FAPbBr$_3$ photoanode at 1.23 V and 0.23 V vs. RHE.

Figure 94. (a) The current of FAPbBr$_3$ photoanode at a constant potential of 1.23 V vs. RHE during Faradaic efficiency measurements. (b) Faradaic efficiencies of FAPbBr$_3$ photoanode for the light-driven OER in 1.0 M KOH.
The ABPE was determined from the corresponding LSV curve in a three-electrode system (Figure 95). For the champion device, a peak ABPE of 8.52% is attained at a potential of 0.082 V vs. RHE. The ABPE value is compared to those reported PEC photoanode systems in Figure 96a. To the best of our knowledge, this ABPE ranks among the highest reported for various photoanodes, including metal oxides, perovskites, polymer bulk heterojunction (BHJ), and silicon-based systems. In contrast to BiVO₄-based photoanodes, which possess a comparable wide band gap, the FAPbBr₃ photoanode markedly excels in achieving a significantly higher ABPE. Furthermore, given the remarkably low potential required to attain this peak ABPE than other narrow band gap perovskites and silicon-based photoanodes, the FAPbBr₃ photoanode emerges as one of the most promising candidates for efficient photo-driven total water splitting.

Figure 95. (a) LSV curve of FAPbBr₃ photoanode in 1.0 M KOH (scan rate: 50 mV s⁻¹). (b) Corresponding ABPE calculated from the LSV curve.

Figure 96b summarizes the best-reported photovoltages for representative PEC and PV devices with divergent band gaps. In PV systems, photovoltage is denoted by the open-circuit potential, while for photoanodes, it is calculated as the difference between the onset potential for photocurrent generation and the Nernstian potential for water oxidation, set at 1.23 V vs. RHE (298 K). Mirroring trends in PV technology, absorbers with a wide band gap (> 2.0 eV) are predicted to achieve photovoltages exceeding 1.4 V, given a free energy loss of 0.6 eV. It is evident that conventional oxide or nitride wide band gap absorbers still have considerable room for photovoltage enhancement. Remarkably, the HTM-free, wide band gap FAPbBr₃ photoanode discussed herein demonstrates the lowest onset potential (approximately –0.12 V) and unprecedented photovoltage (around 1.35 V) among single-junction photoanodes to date. This achievement considerably narrows the photovoltage gap toward the optimal value (>1.6 V). The minimal onset potential substantially eases the specifications for the
counter photocathode, thereby facilitating the development of a cost-effective Z-scheme water splitting system with a solar-to-hydrogen efficiency exceeding 5%. Figure 97 and Table 7 present the $V_{oc}$, photovoltage, and corresponding voltage loss for various perovskite photoanodes designed for water oxidation. In comparison to all other reported photoanodes based on solar cell configurations, which exhibit a voltage loss exceeding 0.2 V, the FAPbBr$_3$ photoanode delivers a markedly lower voltage loss of merely 0.05 V, indicative of optimal internal contact and well-aligned band structure.

Figure 96. (a) ABPE benchmarks of FAPbBr$_3$ photoanodes and other perovskite, BiVO$_4$, BHJ, and Si-based photoanodes. (b) Photovoltage benchmarks for PEC and PV materials as a function of the band gap. Diagonal lines represent the band gap, the Shockley-Queisser (S-Q) photovoltage limit, and the S-Q limit minus 1 V.
Figure 97. Comparison of solar cell $V_{oc}$, photoanode photovoltage, and voltage loss of the reported perovskite photoanodes for water oxidation. Voltage loss is defined as the difference between solar cell $V_{oc}$ and photoanode photovoltage.

Table 7. Photovoltage of the reported perovskite photoanodes for water oxidation.

<table>
<thead>
<tr>
<th>Perovskite composition</th>
<th>Bandgap (eV)</th>
<th>Photovoltage (V)</th>
<th>$V_{oc}$ (V)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA$<em>{0.83}$Cs$</em>{0.17}$Pb(I$<em>{0.8}$Br$</em>{0.2}$)$_3$</td>
<td>1.66</td>
<td>0.7</td>
<td>1.14</td>
<td>385</td>
</tr>
<tr>
<td>MAPbI$_3$</td>
<td>1.5</td>
<td>0.74</td>
<td>1.06</td>
<td>396</td>
</tr>
<tr>
<td>FA$<em>{0.93}$MA$</em>{0.07}$PbI$_3$</td>
<td>1.55</td>
<td>0.73</td>
<td>1.07</td>
<td>384</td>
</tr>
<tr>
<td>CsPbBr$_3$ (2019)$^#$</td>
<td>2.3</td>
<td>0.68</td>
<td>1.31</td>
<td>383</td>
</tr>
<tr>
<td>CsPbBr$_3$ (2023)$^#$</td>
<td>2.3</td>
<td>0.83</td>
<td>1.26</td>
<td>485</td>
</tr>
<tr>
<td>FA$<em>{0.93}$MA$</em>{0.07}$PbI$_3$</td>
<td>1.55</td>
<td>0.8</td>
<td>1.01</td>
<td>486</td>
</tr>
<tr>
<td>FA$<em>{0.80}$MA$</em>{0.15}$Cs$<em>{0.05}$PbI$</em>{2.55}$Br$_{0.45}$</td>
<td>1.57</td>
<td>0.83</td>
<td>1.1</td>
<td>397</td>
</tr>
<tr>
<td>MAPbI$_3$</td>
<td>1.5</td>
<td>0.65</td>
<td>0.98</td>
<td>392</td>
</tr>
<tr>
<td>FAPbBr$_3$$^d$</td>
<td>2.25</td>
<td>1.35$^*$</td>
<td>1.4</td>
<td>This work</td>
</tr>
</tbody>
</table>

# HTM-free device; $^*$Data extract from the device with best ABPE.

5.3 Band structure analysis

To elucidate the underlying factors contributing to the ultralow current onset potential, UPS was employed to illustrate the band alignments of the fabricated devices (Figure 98a). The Fermi level of the FAPbBr$_3$ film is determined to be approximately $-3.7$ eV relative to vacuum, and its valence band energy is measured as $1.9$ eV below the Fermi level (i.e., $-5.6$ eV
relative to the vacuum level), confirming its n-type semiconductor characteristics. DFT calculations were performed to gain a detailed understanding of the energy states and n-type features of the FAPbBr$_3$ material. The lattice parameters and band gap of pristine FAPbBr$_3$ are calculated to be 6.02 Å and 2.41 eV, respectively, which are in close agreement with previously reported experimental values (6.01 Å and 2.3 eV).$^{390, 487, 488}$ Given that the perovskite was synthesized through a two-step process, it is hypothesized that the band structure would predominantly be influenced by non-stoichiometric components, particularly vacancy states. **Figure 98b** presents the calculated total density of states (TDOS) for both pristine and X-site vacancy (V$_{Br}$) perovskites, in which the Fermi energy level of V$_{Br}$ is observed to shift towards the CBM, highlighting the n-type features of Br vacancies due to the presence of donor states within the band gap. The computational findings suggest that the vacancy structure of Br leads to an n-type property of the FAPbBr$_3$ film.

**Figure 98.** (a) UPS spectrum of FAPbBr$_3$ film. (b) Geometric structures and calculated TDOS of pristine and Br-defective FAPbBr$_3$ perovskites. (c) The band alignment structures of FAPbBr$_3$ photoanode under specific conditions.

**Figure 98c** shows the energetic conditions at the n-type FAPbBr$_3$/electrolyte interface. Upon contact between the semiconductor surface and the
electrolyte, thermodynamic equilibrium is established across the interface, resulting in the formation of a depletion layer. Upon light exposure, the quasi-Fermi level for electrons remains aligned with the equilibrium Fermi level, while the quasi-Fermi level for holes experiences a downward shift, approaching the edge of the valence band. The QFLS is intrinsically linked to the open-circuit potential in the PV devices. Given this relationship, the QFLS for the FAPbBr$_3$ layer should be no less than 1.4 eV, as this layer contributes to an open-circuit potential of approximately 1.4 V in the carbon-based PV device. Within the FAPbBr$_3$/electrolyte system, the flat-band potential is approximated as the Fermi level of the FAPbBr$_3$ film, which is $-3.7$ V relative to vacuum. The onset potential for photocurrent can thus be correlated with the flat-band potential. In our investigation, the theoretical onset potential is $E_{\text{onset}} = (3.7 - 4.5) + 0.059 \times 13.6 = 0.02$ V vs. RHE. Concurrently, with a QFLS over 1.4 eV, the oxidation potential for holes exceeding 1.42 V vs. RHE, provides a sufficient overpotential of 0.19 V for apparent water oxidation reactions. More importantly, this theoretical onset potential aligns well with the experimentally measured range of $-0.2$ to 0.1 V vs. RHE, as presented in Figure 93b, which confirms that the ultralow onset potential in the FAPbBr$_3$ photoanode originates from a shallower Fermi level and an elevated photovoltage. These findings underscore the pivotal role of the Fermi level and semiconductor band structure alignment in engineering high-efficiency, low-overpotential photoanodes.

### 5.4 Stability of photoanode

While both NiFe-based catalysts and HTM-free FAPbBr$_3$ solar cells have demonstrated robust stability under operational conditions, ensuring long-term stability for integrated photoelectrodes in the corrosive electrolytic environment remains challenging. The catalytic stability of FAPbBr$_3$ photoanodes was studied via chronoamperometry in 1.0 M KOH solutions. The device exhibits a current half-life exceeding 55 hours, outperforming all other systems listed in Figure 99a. Remarkably, the current exhibits no degradation during the first 12 hours of illumination and retains approximately 95% of its initial value after a 24-hour operational period. Inset images in Figure 99a show the PEC cell upon 24 and 55 hours of photo-electrolysis; the orange active area of the photoanode progressively whitens over time, coinciding with the diminishing photocurrent, indicative of the gradual degradation of the encapsulated perovskite layer.
Figure 99. Normalized chronoamperometric measurement of FAPbBr$_3$ photoanode at 1.23 V vs. RHE in 1.0 M KOH solutions under (a) standard AM 1.5G illumination and (b) filtered AM 1.5G illumination. (c) LSV curves of FAPbBr$_3$ photoanode with different filters in 1.0 M KOH (scan rate: 50 mV s$^{-1}$). (d) The proposed UV degradation mechanism for FAPbBr$_3$ photoanode.

The subsequent investigation focused on identifying possibilities for enhancing the stability of degraded photoanodes. For this purpose, deactivated photoanodes were disassembled to examine the underlying
degradation mechanisms. As illustrated in Figure 100b, the evaluated sample could be readily separated into two parts, revealing that the graphite/carbon layer detached from the glass substrate. SEM was utilized to investigate the interface between these two separated components. Figure 100a indicates that the perovskite layer firmly adhered to the carbon layer. In stark contrast, only a minor fraction of the perovskite crystal is found affixed to the ITO glass substrate, as depicted in Figure 100c. In the case of a nondegraded sample, the ITO glass substrate should exhibit an orange color due to the growth of the FAPbBr$_3$ layer. However, post-testing reveals that the FAPbBr$_3$ layer has detached from the substrate, leaving the latter transparent.

Figure 100. (a) SEM images for the carbon part of tested FAPbBr$_3$ photoanode in oblique view. (b) Schematic diagram of the photoanode degradation process and digital images of pristine and tested FAPbBr$_3$ photoanode. (c) SEM images for the glass part of tested FAPbBr$_3$ photoanode in cross-section view.
The stability of lead halide perovskite solar cells is affected by various external factors, such as heat, moisture, voltage, and UV light. Among these, UV light exposure presents a unique challenge, largely attributed to the photocatalytic effects of electron-transport materials like TiO₂ and SnO₂, which are primary contributors to perovskite degradation. The theoretical oxidation potential of bromine anion (Br⁻) is 1.087 V vs. NHE, equivalent to −5.59 eV with respect to the vacuum level. This potential closely aligns with the VBM of FAPbBr₃ perovskite. Therefore, under visible light irradiation, the oxidation of Br⁻ ions by excited holes is improbable in FAPbBr₃, as it necessitates an additional driving force. However, as illustrated in Figure 99d, highly oxidative holes tend to accumulate at the SnO₂/perovskite interface upon UV exposure. These accumulated charges are capable of extracting electrons from the Br⁻ ions within the SnO₂/FAPbBr₃ junction, thereby destabilizing the perovskite interface and leading to the formation of monomers (FABr or PbBr₂).

To corroborate the detrimental impact of UV light on the device stability, systematic tests were carried out employing a long-pass UV filter with a cut-off wavelength greater than 400 nm, as well as a bandpass visible light filter ranging from 200 to 400 nm. Figure 99c illustrates that under UV-filtered illumination, the photocurrent of the FAPbBr₃ photoanode experiences a reduction of approximately 25%, decreasing to about 7.0 mA cm⁻² at 1.23 V vs. RHE. Upon the application of a visible light filter, the photocurrent is restricted to 1.23 mA cm⁻² at 1.23 V vs. RHE. Furthermore, the onset potential experienced a substantial upshift in the presence of pure UV light, which can be attributed to the limited penetration of UV light into the perovskite film, thereby offering inadequate driving force for carrier mobility towards the HTM side. Figure 99b shows the stability measurements conducted under filtered light conditions. The FAPbBr₃ photoanode exhibits rapid degradation under UV light, possessing a current half-life of merely 2.2 hours, thereby substantiating the sensitivity of the perovskite system to UV light. Concurrently, the color transformation of the FAPbBr₃ layer to white indicates accelerated degradation at the ITO-SnO₂/FAPbBr₃ interface. Conversely, in the absence of UV light, the photoanode maintains its exceptional stability, retaining nearly 100% of its initial photocurrent for 50 operational hours and subsequently decaying to 88% over an additional 24-hour period. Notably, the photocurrent is fully restored after a 12-hour dark-rest period under open-circuit conditions, a characteristic commonly observed in conventional n-i-p structured perovskite solar cells.

The system demonstrates remarkable operational stability, experiencing no current decay even after a cumulative 96 hours of electrolysis, and retains over 57% of its initial photocurrent density upon 125 hours of operation. As
indicated in the inset of Figure 99b, this reduction in current is attributed to a sealing failure allowing moisture penetration at the edges, suggesting that enhancements in sealing materials and techniques could further enhance device stability. To the best of our knowledge, the fabricated FAPbBr3 photoanode represents the first example of a lead halide perovskite-based photoanode achieving stability beyond 100 hours to date, with almost no performance decay (Table 8). While the employment of a UV filter incurs a performance decrement, the saturation current, ranging between 7 and 8 mA cm−2, still surpasses that of oxide-based photoanodes, such as BiVO4 and WO3, rendering the encapsulated FAPbBr3 perovskite a competitive photoanode material.

Table 8. Stability of the reported perovskite photoanodes for water oxidation.

<table>
<thead>
<tr>
<th>Perovskite composition</th>
<th>Year</th>
<th>Stability data (Operation time/residual current)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPbI3</td>
<td>2016</td>
<td>0.5 h/64%</td>
<td>396</td>
</tr>
<tr>
<td>MAPbI3</td>
<td>2018</td>
<td>6 h/0%</td>
<td>392</td>
</tr>
<tr>
<td>(5−AVA)x(MA)1−xPbI3#</td>
<td>2019</td>
<td>12 h/69%</td>
<td>394</td>
</tr>
<tr>
<td>FA0.80MA0.12Cs0.05PbI2.55Br0.45</td>
<td>2021</td>
<td>13 h/84%</td>
<td>397</td>
</tr>
<tr>
<td>CsPbBr3#</td>
<td>2019</td>
<td>35 h/7%</td>
<td>383</td>
</tr>
<tr>
<td>CsPbBr3#</td>
<td>2023</td>
<td>24 h/78% 70 h/77%</td>
<td>485</td>
</tr>
<tr>
<td>FA0.83Cs0.17Pb(I0.8Br0.2)3</td>
<td>2021</td>
<td>47 h/0%</td>
<td>385</td>
</tr>
<tr>
<td>FA0.93MA0.07PbI3</td>
<td>2022</td>
<td>12 h/86% 48 h/50%</td>
<td>384</td>
</tr>
<tr>
<td>FAPbBr3#</td>
<td>2023</td>
<td>12 h/100% 24 h/94% 60 h/43%</td>
<td>This work</td>
</tr>
<tr>
<td>FAPbBr3# (UV filter)</td>
<td>2023</td>
<td>100 h/95% 125 h/57%</td>
<td>This work</td>
</tr>
</tbody>
</table>

# HTM-free device.

5.5 Conclusions

In summary, this chapter has successfully demonstrated a FAPbBr3-based photoanode, characterized by a photocurrent density of approximately 8.5 mA cm−2 at 1.23 V vs. RHE, an onset potential lower than 0 V vs. RHE, and a half-life stability exceeding 55 hours. This performance was achieved by integrating a FAPbBr3 absorber, a carbon/graphite conductive protection layer, a NiFe alloy/NiFe LDH catalyst, and edge protection by resin epoxy. With rapid catalytic kinetics, high photovoltage, and optimized band structure, an impressive ABPE of 8.5% is attained at 0.08 V vs. RHE. Subsequent stability assessments and post-analyses indicate that UV light adversely affected the perovskite interface, causing the absorber layer to detach and resulting in performance degradation. Subsequently, the
incorporation of a UV filter enables the device to achieve unprecedented stability of over 100 hours under continuous simulated solar illumination, sustaining a current density of approximately 7.5 mA cm\(^{-2}\) at 1.23 V vs. RHE. The as-fabricated FAPbBr\(_3\) photoanode is notably straightforward to synthesize through solution-based methods, obviating the need for high temperatures, inert atmospheres, or vacuum evaporation techniques. The carbon/GS protective approach effectively shields the perovskite from water-induced corrosion; the absence of HTM and precious metals significantly diminishes production costs. Furthermore, the well-established, scalable electrodeposition technique for catalyst layer fabrication enables facile manipulation of electrocatalyst composition, structure, and morphology. The compact design endows the monolithic device with outstanding portability and stability, coupled with the remarkably low onset potential and the facile processability of the FAPbBr\(_3\) photoanode; these findings highlight the considerable promise of lead halide perovskite-based PEC systems as a viable pathway toward efficient, economical, and scalable solar fuel generation.
This thesis details our endeavors to develop efficient (photo)electrochemical water oxidation systems, focusing on two main aspects: catalysis and light harvesting.

Chapter 3 presents the successful fabrication of the Co@CB[5] host-guest complex, serving as a supramolecular WOC. Once anchored to the conductive ITO surface, this Co@CB[5] complex demonstrates significant electrochemical activity for water oxidation. Further kinetic evaluations validate that this supramolecular WOC enhances surface charge transfer rates while suppressing surface charge recombination in the BiVO₄ photoanode. However, the lack of clarity in the catalyst molecular structure obstructs insights into its catalytic mechanism, and the device's performance falls short of commercial expectations that STH efficiency exceeds 10% (i.e., operation current higher than 8.13 mA cm⁻² when assuming 100% catalytic faraday efficiency). Through these limitations, we discerned the necessity of new, well-defined molecular models when investigating the water oxidation mechanism. Moreover, the inherent limitations of current oxide-based semiconductor materials constrain the further enhancement of PEC device performance. This underscores the need for innovation in light-absorbing materials and device structure optimization.

For these reasons, Chapter 4 focuses on the synthesis and detailed characterization of well-defined single cobalt sites, with an aim to shed light on the O-O bond mechanisms underlying single-site heterogeneous water oxidation. These single cobalt sites within Aza-CMP-Co show remarkable activity across both alkaline and near-neutral conditions. In-depth investigations indicate that the cobalt sites facilitate a pH-dependent nucleophilic attack pathway during water oxidation. Specifically, at higher pH values, an additional hydroxyl group, resulting from the non-concerted PCET process of Co²⁺ to Co³⁺ redox, favors the formation of the Co-OOH fragment via an intramolecular hydroxyl nucleophilic attack pathway that requires considerably less activation energy than its intermolecular WNA counterpart. Meanwhile, diffusion-controlled interfacial proton transfer and endothermic O-H bond cleavage processes are not involved in the RDS of this IHNA pathway, which leads to faster reaction kinetics. Consequently, Aza-CMP-Co achieves a notable TOF of 0.95 s⁻¹ at an overpotential of 300 mV under alkaline conditions, which further increased to 10.6 s⁻¹ at 350 mV.
Such insights clarify the pronounced drop in performance observed when transitioning from an alkaline medium to a near-neutral one. This work emphasizes the critical role of electrolyte pH in water oxidation catalysis and paves the way for further explorations in heterogeneous (photo)electrocatalytic systems featuring atomically dispersed active centers.

**Chapter 5** explores the prospective application of the novel light-absorbing material, FAPbBr$_3$, as a promising candidate for developing perovskite-based photoanodes for photoelectrochemical water oxidation. Highlighting the notable electronic and optical properties of FAPbBr$_3$, a precious metal-free photovoltaic device with a planar structure was fabricated using mesoporous carbon as the hole-conducting layer, which achieves a PCE of 9.2% and an open-circuit voltage of 1.4 V. Leveraging this design, a monolithic photoanode was developed, integrating the FAPbBr$_3$ absorber, carbon/graphite conductive protection layers, and NiFe catalyst layers. Remarkably, this photoanode demonstrates a saturation current density over 8.0 mA cm$^{-2}$, an onset potential below 0 V vs. RHE, and a notable ABPE of 8.5%. Given the good stability of perovskites combined with effective encapsulation strategies, this work marks, to our understanding, the first instance of a perovskite-based photoanode achieving stable operation for over 100 hours under solar illumination. The compact, HTM-free, precious metal-free design and the facile processability, combined with superior performance surpassing the top-performing oxide-based photoanodes, underscore the huge potential of lead halide perovskite-based photoelectrodes in achieving efficient, affordable, and scalable photoelectrochemical solar fuel production.

With ongoing advancements in water oxidation catalysts and an in-depth understanding of the water oxidation mechanism, coupled with persistent research into high-efficiency light-absorbing materials, it is evident that efficient, durable, cost-effective, and scalable (photo)electrochemical water splitting systems will become indispensable for future energy solutions.
Solar energy, given its vast supply and eco-friendly nature, emerges as a promising prospect in the search for alternative energy sources. One of the most efficient strategies for harnessing this renewable power is through artificial photosynthesis, which converts sunlight directly into chemical energy. The concept of solar-driven water splitting for sustainable hydrogen generation has been intensively examined over the last several decades using PV-EC methods, PEC systems, and particulate photocatalysts. However, the advancement of artificial photosynthesis devices to practical, large-scale applications necessitates improvements, targeting STH efficiencies surpassing 10%, prolonged lifetime on the scale of years, enhanced scalability reaching km² magnitudes, and a more economical hydrogen production cost than conventional approaches.

The water oxidation reaction serves as an optimal anodic process, supplying the requisite electrons and protons for hydrogen production, as well as reductions of CO₂ and N₂. Despite its importance, the water oxidation process is hindered by its intrinsically slow kinetics, largely attributable to the complex processes of extracting four protons and electrons from two water molecules, the breaking of O-H bonds, and the subsequent formation of O-O bonds. A comprehensive understanding of the water oxidation mechanism, in conjunction with studying the structure-function relationship in catalysts, is crucial for advancing water splitting systems. Polymeric materials with well-defined structures, like COFs, exhibit a combination of stability, chemical versatility, and flexibility in metal site incorporation, making them prime candidates for both lab-scale WOC exploration and potential industrial uses. We anticipate that steering molecularly defined heterogeneous WOCs in this direction could bridge the insights from molecular WOCs to practical heterogeneous electrocatalytic devices (Figure 101b).

In the field of PV-EC and PEC water splitting, the development of efficient, durable, and cost-effective light-absorbing materials has proven to be very demanding. The research presented in this thesis shows the significant potential of organic-inorganic hybrid lead halide perovskite-based photoelectrodes for achieving scalable solar fuel production. Through rational compositional and structural strategies addressed in this thesis, there has been a remarkable enhancement in the performance and stability of PVM-PEC systems. The findings further indicate that the high band gap
FAPbBr₃ perovskite material holds high potential for applications within solar cell and photoelectrochemical cell fields. With the persistent in-depth exploration of third-generation PV technologies, we are confident that continued research into PV material-based photoelectrodes, especially organic-inorganic hybrid MHPs, offers a promising pathway for sustainable, industrial-scale solar fuel production (Figure 101a). Ultimately, integrating insights across molecules to materials and bridging the gap between organic and inorganic domains, combined with cross-disciplinary collaboration, has the potential to uncover unforeseen breakthroughs.

**Figure 101.** (a) Light absorbers can be grouped into three main categories: organic (or metalorganics) systems, inorganic systems, and hybrid systems that integrate both organic and inorganic components. (b) WOCs can be categorized into three primary types: molecular systems, material-based systems, and hybrid systems that combine both molecular and material features.
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Appendix

The following is a description of the author's contributions to Publications I to III, as requested by KTH:

**Paper I**: Hao Yang, Fusheng Li, and Licheng Sun conceived the project design and initiated the project. Hao Yang performed material synthesis, most structural characterization, and electrochemical measurements. All spectra and electrochemical kinetics data were analyzed and interpreted by Hao Yang and Fusheng Li. Qiming Zhuo and Dinghua Zhou performed the SEM measurements. All authors contributed to the discussions. Xiujuan Wu, PeiLi Zhang, and Zhaoyang Yao contributed to data analysis and interpretation. Fusheng Li wrote the original draft with inputs from the other authors, and Hao Yang and Licheng Sun revised the manuscript. All authors reviewed the paper. Licheng Sun and Fusheng Li supervised the research.

**Paper II**: Hao Yang, Fusheng Li, and Licheng Sun conceived the project design and initiated the project. Hao Yang performed catalyst synthesis, most structural characterization, and electrochemical measurements. All spectra and electrochemical kinetics data were analyzed and interpreted by Hao Yang and Fusheng Li. Shaoqi Zhan and Mårten S. G. Ahlquist performed DFT calculations. Yawen Liu and Hao Yang performed FT-IR, XRD, and XPS measurements and data analysis. Wenlong Li performed Raman measurements and data analysis. Yi Yang performed ICP-OES measurements and data analysis. Yuan Fang and István Furó performed SS-NMR measurements and data analysis. Linqin Wang and Jiaqi Guan performed STM measurements and data analysis. All authors contributed to the discussions. Hao Yang wrote the original draft with inputs from the other authors, and Fusheng Li and Licheng Sun revised the manuscript. All authors reviewed the paper. Licheng Sun supervised the research.

**Paper III**: Hao Yang, Yawen Liu, Erik M. J. Johansson, and Licheng Sun conceived the project design and initiated the project. Hao Yang and Yawen Liu performed synthesis, structural, and electrochemical characterizations. Yunxuan Ding performed DFT calculations. Hao Yang, Yawen Liu, Fusheng Li, Linqin Wang, Bin Cai, Fuguo Zhang, Tianqi Liu, and Gerrit Boschloo contributed to data analysis and interpretation. All authors contributed to the discussions. Hao Yang and Yawen Liu wrote the original draft with inputs from the other authors, and all authors reviewed and revised the manuscript. Erik M. J. Johansson and Licheng Sun supervised the research.
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