Surface Modification of Photoelectrodes for Photoelectrochemical Water Splitting

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Diese Dissertation ist auf den Internetseiten der Universitätsbibliothek verfügbar.
Dedication

* Dedicated to my beloved parents. 
“三人行，必有我师焉。”
《论语》——孔子

“When three men meet together, one of them who is anxious
to learn can always learn something of the other two.”

*Analects of Confucius*
Abstract

Utilizing solar energy to produce clean and renewable energy is an attractive route to solve the two major restriction factors i.e. the growing pollution of environment and energy shortage. A photoelectrochemical (PEC) cell, which can absorb sufficiently solar energy to split abundant water into the energy carrier hydrogen, has proven to be an encouraging technology to address both the energy demand and environment problems of water and air pollution. The semiconducting photoelectrodes and the cocatalysts serving as the two main components of PEC devices are indispensable to achieve sufficiently water splitting efficiency. Keeping in line with these goals, different semiconducting photoabsorbers and cocatalysts have been investigated in this thesis.

In chapter 2, the ternary metal oxide CuWO$_4$ with a band gap of 2.2–2.4 eV has been prepared as a thin film photoanode for PEC water oxidation and the performance has been augmented by a facile post-annealing under nitrogen atmosphere at 623 K for 3.5 h. The post-treated CuWO$_4$ exhibits a photocurrent of 80 μA cm$^{-2}$ at 1.23 V versus reversible hydrogen electrode (RHE) under Air Mass 1.5 Global (AM 1.5G) illumination in a phosphate buffer electrolyte at pH 7, almost three times higher when comparing to the pristine photoanode. Physical characterization indicates that post-annealing of the CuWO$_4$ thin films in a N$_2$ atmosphere does not introduce nitrogen into the crystal structure, thus no bathochromic shift is observed. The greater concentration of oxygen vacancies, which can improve charge carrier separation and reduce the charge transfer resistance, has been proposed the reasons of superior PEC water oxidation performance.

In chapter 3, a quaternary oxynitride nanowire SrTaO$_2$N thin film has been used as the core photoabsorber to construct a core-shell structure with functional overlayers for PEC water oxidation. The perovskite-related oxynitride structure is obtained by converting the hydrothermally grown oxide precursor on tantalum substrate via nitridation. The performance of the as-prepared nanowire SrTaO$_2$N has been enhanced by the deposition of three functional overlayers. The first TiO$_x$ layer can protect the oxynitride from photocorrosion and suppress the recombination of charge carrier at the surface. A hole-storage layer Ni(OH)$_x$ can decrease the dark-current, leading to a significantly improved extraction of photogenerated holes to the electrode-electrolyte surface. The cocatalyst cobalt phosphate layer can increase the photocurrent up to 0.27 mA cm$^{-2}$ at 1.23 V versus RHE under AM 1.5G illumination. The common dark current in case of oxynitride photoanodes grown on metallic substrates has been minimized almost to zero.

In chapter 4, the tailoring of the surface properties of quaternary tantalum-based oxynitrudes ATa(O,N)$_3$ is critical to obtain efficient hole extraction. A cubic CaTaO$_2$N particle-based photoanode has been altered by acidic treatment for PEC water oxidation. The acidic etching effect has been addressed by means of complementary physical characterization
techniques, such as X-ray photoelectron spectroscopy, electrochemical impedance spectroscopy, \(^1\)H and \(^{14}\)N solid-state nuclear magnetic resonance (NMR) spectroscopy, and electron microscopy. Combining with PEC measurements, solid-state NMR indicates that the restructured surface displays a meaningfully higher concentration of terminating OH groups. The deposition of the cocatalyst nickel borate on the etched surface yields a higher percentual upsurge of photocurrent in comparison to pristine CaTaO\(_2\)N. The work in this chapter highlights the application of solid-state NMR spectroscopy for understanding the semiconductor-catalyst interface in photochemical devices.

In chapter 5, a trivalent iron-only layered oxyhydroxide mössbauerite has been investigated as cocatalyst for PEC water oxidation by coupling with a WO\(_3\) semiconductor photoanode. By combining Mott-Schottky analysis and UV-Vis diffuse reflectance spectroscopy, the band edge positions of mössbauerite have been determined. Mössbauerite is identified to be a n-type semiconductor with a flat band potential of 0.34 V versus RHE. However, the bare mössbauerite does not produce noticeable photocurrent during water oxidation. By constructing a type-II heterojunction with WO\(_3\) thin films photoanode, the charge carrier separation is amended and a photocurrent of up to 1.22 mA cm\(^{-2}\) at 1.23 V versus RHE is achieved.

In chapter 6, the monodisperse spherical alloy FePt and pure Pt nanocrystals as cocatalysts have been used to modify p-WSe\(_2\) single-crystal photocathodes. The photocurrents of −0.27 and −4.0 mA cm\(^{-2}\) at 0 V versus RHE, which are 7.4 and 15 times higher compared to pristine WSe\(_2\) single crystal, are achieved for the hydrogen evolution reaction (HER) after the modification with Pt or FePt, respectively. The density functional theory computations reveal that the water adsorption and thus enhanced H\(_2\)O dissociation are preferential on FePt in comparison to Pt. The edge sites of both Pt and FePt are the preferential sites for hydrogen production because of a more negative adsorption energy than on the (111) and (100) facets. The size of the Pt nanocrystal within the range of Pt\(_{55}\) (1.1 nm) and Pt\(_{147}\) (1.6 nm) does not significantly influence the mechanism for the HER, as revealed by computational results.
Zusammenfassung


In Kapitel 3 wurde das quaternäre Oxidonitrid SrTaO₂N in der Form von Nanodrähten ab Photoabsorber verwendet, um eine Kern-Schale-Struktur mit funktionellen Beschichtungen für die photoelektrochemische Wasseroxidation aufzubauen. Die Perowskitt-verwandte Oxidonitridstruktur wird erhalten, indem der hydrothermal hergestellte Oxidvorläufer durch Nitridierung auf einem Tantalsubstrat umgewandelt wird. Die Effizienz der Wasserspaltung des so hergestellten Nanodrahtes SrTaO₂N wurde durch die Abscheidung von drei funktionellen Überzügen verbessert. Die erste TiOₓ-Schicht kann das Oxidonitrid vor Photokorrosion schützen und die Rekombination der Ladungsträger an der Oberfläche unterdrücken. Eine Lochspeicherschicht Ni(OH)ₓ kann den Dunkelstrom verringern, was zu einer signifikant verbesserten Extraktion von photogenerierten Löchern auf der Elektrodenoberfläche führt. Die Cobaltphosphatschicht als Katalysator kann den Photostrom bei 1,23 V gegenüber RHE unter AM1,5G-Beleuchtung auf 0,27 mA cm⁻² erhöhen. Der übliche Dunkelstrom von Oxidonitrid-Photoanoden wurde nahezu auf null minimiert.
In Kapitel 4 ist die Anpassung der Oberflächeneigenschaften der quaternären Oxidinitride ATa(O, N)₃ auf Tantalbasis entscheidend, um eine effiziente Lochextraktion zu erzielen. Eine Photoanode auf CaTaO₂N-Partikelbasis wurde durch Säurebehandlung für die PEC-Wasseroxidation verändert. Der Ätzeffekt wurde mittels komplementärer physikalischer Charakterisierungstechniken wie Röntgenphotoelektronenspektroskopie, elektrochemischer Impedanzspektroskopie, ¹H- und ¹⁴N-Festkörper-Kernspinresonanzspektroskopie (NMR) und Elektronenmikroskopie untersucht. Die umstrukturierte Oberfläche weist eine deutlich höhere Konzentration an terminierenden OH-Gruppen auf. Die Abscheidung eines Nickelboratkatalysators auf der geätzten Oberfläche führt zu einem höheren prozentualen Anstieg des Photostroms im Vergleich zu unbehandeltem CaTaO₂N. Die Arbeit in diesem Kapitel zeigt die Anwendung der Festkörper-NMR-Spektroskopie zum Verständnis der Grenzfläche zwischen Halbleiter und Katalysator in photochemischen Bauelementen.


In Kapitel 6 wurden die monodispersen FePt- und Pt-Nanokristalle als Katalysatoren verwendet, um die p-WSe₂-Einkristall-Photokathoden zu modifizieren. Die Photoströme von −0,27 und −4,0 mA cm⁻² bei 0 V gegenüber RHE, die 7,4- und 15-mal höher sind als bei einem unmodifizierten WSe₂-Einkristall, werden für die Wasserstoffentwicklungsreaktion (HER) nach der Modifikation mit Pt bzw. FePt erreicht. Berechnungen mit der Dichtefunktionaltheorie zeigen, dass die Wasseradsorption und damit die verstärkte H₂O-Dissoziation gegenüber FePt im Vergleich zu Pt bevorzuge sind. Die Kanten von Pt- und FePt-Nanokristallen sind aufgrund einer negativeren Adsorptionsenergie die bevorzugten Stellen für die Wasserstoffproduktion im Vergleich zu den (111) und (100) Ebenen. Die Größe des Pt-Nanokristalls im Bereich von Pt₅₅ (1,1 nm) und Pt₁₄₇ (1,6 nm) beeinflusst den Mechanismus für HER nicht signifikant, wie aus den Berechnungsergebnissen hervorgeht.
The work presented in the thesis was carried out at the Institute of Inorganic Chemistry of RWTH Aachen University between September 2017 and October 2020 under the supervision of Prof. Dr. Richard Dronskowski and Prof. Dr. Adam Slabon.

I, Zili Ma

declare that this thesis and the work presented in it are my own and has been generated by me as the result of my own original research.

I do solemnly swear that:

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Date: 28 October 2020

Zili Ma
Publications

Parts of this thesis have been published or are in the process of being published:


Other publications:


# = equal contributions
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<th>Description</th>
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<tbody>
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<td>AM 1.5G</td>
<td>Air Mass 1.5 Global</td>
</tr>
<tr>
<td>AR5</td>
<td>the Fifth Assessment Report</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society of Testing and Materials</td>
</tr>
<tr>
<td>a.u.</td>
<td>arbitrary unit</td>
</tr>
<tr>
<td>CA</td>
<td>chronoamperometry</td>
</tr>
<tr>
<td>CB</td>
<td>conduction band</td>
</tr>
<tr>
<td>COHP</td>
<td>Crystal Orbital Hamilton Population technique</td>
</tr>
<tr>
<td>CoP&lt;sub&gt;i&lt;/sub&gt;</td>
<td>cobalt phosphate</td>
</tr>
<tr>
<td>CVT</td>
<td>chemical vapor transport</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>EDX</td>
<td>energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EELS</td>
<td>electron energy-loss spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>ELNES</td>
<td>energy-loss near-edge fine structure</td>
</tr>
<tr>
<td>FTO</td>
<td>fluorine-doped tin oxide</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier-transform infrared spectroscopy</td>
</tr>
<tr>
<td>fwhm</td>
<td>full width at half maximum</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>ICOHP</td>
<td>integrated Crystal Orbital Hamilton Population</td>
</tr>
<tr>
<td>ICSD</td>
<td>inorganic crystal structure database</td>
</tr>
<tr>
<td>IPCC</td>
<td>the Intergovernmental Panel on Climate Change</td>
</tr>
<tr>
<td>IPCE</td>
<td>incident photon to converted electron</td>
</tr>
<tr>
<td>KB&lt;sub&gt;i&lt;/sub&gt;</td>
<td>potassium borate</td>
</tr>
<tr>
<td>KP&lt;sub&gt;i&lt;/sub&gt;</td>
<td>potassium phosphate</td>
</tr>
<tr>
<td>LDH</td>
<td>layered double hydroxides</td>
</tr>
<tr>
<td>LSV</td>
<td>linear sweep voltammetry</td>
</tr>
<tr>
<td>MAS</td>
<td>magic angle spinning</td>
</tr>
<tr>
<td>MLSVD</td>
<td>multilinear single-value decomposition</td>
</tr>
<tr>
<td>NCs</td>
<td>nanocrystals</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>NHE</td>
<td>normal Hydrogen Electrode</td>
</tr>
<tr>
<td>NiB</td>
<td>nickel borate</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
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<tr>
<td>OER</td>
<td>oxygen evolution reaction</td>
</tr>
<tr>
<td>PAW</td>
<td>projector augmented wave</td>
</tr>
<tr>
<td>PBE</td>
<td>Perdew-Burke-Ernzerhof</td>
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<tr>
<td>PDOS</td>
<td>projected density of states</td>
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<tr>
<td>PEC</td>
<td>photoelectrochemical</td>
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<tr>
<td>PXRD</td>
<td>powder X-ray Diffraction</td>
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<tr>
<td>RHE</td>
<td>reversible hydrogen electrode</td>
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<tr>
<td>SAEDP</td>
<td>selected-area electron diffraction pattern</td>
</tr>
<tr>
<td>SCR</td>
<td>space charge region</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>STEM</td>
<td>scanning transmission electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TMDCs</td>
<td>transition metal dichalcogenides</td>
</tr>
<tr>
<td>UNEP</td>
<td>the United Nations Environment Program</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>UV-vis</td>
<td>ultraviolet-visible</td>
</tr>
<tr>
<td>VASP</td>
<td>Vienna ab initio simulation package</td>
</tr>
<tr>
<td>VB</td>
<td>valence band</td>
</tr>
<tr>
<td>WMO</td>
<td>World Meteorological Organization</td>
</tr>
<tr>
<td>XP</td>
<td>X-ray photoelectron</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy/spectra</td>
</tr>
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<table>
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<th>Definition</th>
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<tbody>
<tr>
<td>$A$</td>
<td>area</td>
</tr>
<tr>
<td>$B_0$</td>
<td>magnetic field</td>
</tr>
<tr>
<td>$C$</td>
<td>interfacial capacitance</td>
</tr>
<tr>
<td>$C_{\text{bulk}}$</td>
<td>the bulk capacitance of thin film</td>
</tr>
<tr>
<td>$C_{\text{ss}}$</td>
<td>the surface-state capacitance</td>
</tr>
<tr>
<td>$e$</td>
<td>electronic charge</td>
</tr>
<tr>
<td>$E$</td>
<td>potential</td>
</tr>
<tr>
<td>$E_b$</td>
<td>binding energy</td>
</tr>
<tr>
<td>$E_F$</td>
<td>Fermi energy</td>
</tr>
<tr>
<td>$E_{\text{fb}}$</td>
<td>flat band potential</td>
</tr>
<tr>
<td>$E_g$</td>
<td>band gap</td>
</tr>
<tr>
<td>$e_0$</td>
<td>the electron charge</td>
</tr>
<tr>
<td>$h$</td>
<td>Planck constant</td>
</tr>
<tr>
<td>$I$</td>
<td>current</td>
</tr>
<tr>
<td>$J_{\text{max}}$</td>
<td>theoretical maximum photocurrent</td>
</tr>
<tr>
<td>$J_{\text{sulfite}}$</td>
<td>the maximal photocurrent in sulfite electrolyte</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann’s constant</td>
</tr>
<tr>
<td>$N_{AV}$</td>
<td>average coordination number</td>
</tr>
<tr>
<td>$N_D$</td>
<td>the number of donors</td>
</tr>
<tr>
<td>$N_s$</td>
<td>number of surface atoms</td>
</tr>
<tr>
<td>$R_{\text{ct,ss}}$</td>
<td>the charge-transfer resistance at the surface-electrolyte interface</td>
</tr>
<tr>
<td>$R_{\text{ed}}$</td>
<td>the ratio of atoms at edges to atoms at surfaces</td>
</tr>
<tr>
<td>$R_s$</td>
<td>the resistance from the bulk thin film, the electrolyte, and the electrical contacts</td>
</tr>
<tr>
<td>$R_{\text{trap}}$</td>
<td>the resistance of trapped electrons at the surface</td>
</tr>
<tr>
<td>$T$</td>
<td>absolute temperature</td>
</tr>
<tr>
<td>$V$</td>
<td>potential</td>
</tr>
<tr>
<td>$V_H$</td>
<td>the potential drop across the Helmholtz layer</td>
</tr>
<tr>
<td>$\Delta E_F$</td>
<td>the difference between the Fermi level and the majority charge carrier band</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>the dielectric constant</td>
</tr>
<tr>
<td>$\eta_{\text{abs}}$</td>
<td>the absorption efficiency</td>
</tr>
</tbody>
</table>
1 Introduction

1.1 Environment, Energy and Sunlight

The rapid increasing in prosperity in the world is driving a high demand of energy. As reported in BP Statistical Review of World Energy of 2019, the growth rate of primary energy consumption in 2018 is 2.9%, which is almost double its 10-year average of 1.5 per year and the fastest since 2010. Among the different fuel types, the fossil fuels are still the most critical ones to the development of modern society; a percentage 84.7% of the total energy consumption is reached in 2018 (see Figure 1.1.1). In the future, more energy consumption will be demanded due to industrialization in underdeveloped and developing countries coupled with increasing world population. Although the fossil fuels are forming via natural processes, they generally take millions of years. The known viable reserves could only meet the future energy demand at the expected consumption rate for at least several centuries, as stated in the World Energy Assessment Report: Energy and the Challenge of Sustainability.

![Figure 1.1.1 Percentage world primary energy consumption by fuel type in 2018. Data adapted from BP Statistical Review of World Energy of 2019 in Ref 1.](image)

One of the scientific grand challenges of humans is to meet the pressing energy demand in a sustainable route. First, nuclear energy (fission and fusion) is expected to form a solid basis of tomorrow's energy demands, in particular by generation IV technology. Second, the renewable energy, which is hoped to be environmental-friendly and gives zero carbon dioxide emission, is an alternative candidate to replace fossil fuels. The renewable energy includes different types such as wind energy, geothermal energy, hydropower and solar energy. The latter like photovoltaics and solar heating can directly convert sunlight to electricity or heat. The sun is the largest and inexhaustible energy resource at no cost suppling
for earth. It can provide more energy in 1 hour to the earth than the total energy consumption of humans in an entire year.³ Hence, electricity prices in environmentally punitive Germany have skyrocketed and continue to do so. However, the diurnal, seasonal and intermittent cloud cover nature of sunlight limit the application of photovoltaics because it requires a constant source of sunlight irradiation. Another limitation is the diffuse nature of solar energy. Therefore, exploring a dispatchable solar-based energy system would be a worthy goal to strive for.

Hydrogen is widely used to synthesize ammonia via the Haber-Bosch process and chemically reduce CO₂ to produce carbon-based fuels such as methanol and methane. Except that, hydrogen is an excellent energy carrier with high energy density as a replacement of fossil fuels but also difficult to store. The hydrogen can be used as energy carrier in several ways such as chemical fuel in an internal combustion engine and in a fuel cell to generate electricity. Water is the only product when hydrogen is combusted. Hence, hydrogen is indeed an attractive alternative to fossil fuels to meet the global energy demand when taking the previously mentioned advantages into account. However, ca. 96 % of world hydrogen is currently produced via steam-methane reforming and the water-gas shift reaction. This process not only relies on fossil fuels but also emits significant amount of CO₂ into the environment.⁴ Thus, exploring a clean and sustainable production method of hydrogen is an attractive research area. Considering the inexhaustible advantage and the intermittent disadvantage of solar energy, storing the solar energy into the hydrogen as chemical bonds looks like an appealing approach to solve the worldwide energy problems. The stored energy can be released back in a controlled manner when it is needed. The best reaction to store the solar energy into hydrogen bonds is splitting water into H₂ and O₂ by using sunlight. PEC water splitting is one of the most feasible and promising approaches to collect and convert solar energy into chemical bonds.⁵

1.2 Photoelectrochemical Water Splitting

The pioneering work by Fujishima and Honda in 1972 was established on a PEC water splitting cell based on TiO₂.⁶ After that, PEC technology has been extensively investigated for hydrogen production, CO₂ utilization⁷ and glycerol oxidation⁸. A PEC system contains spatially separated anodic and cathodic half-reactions. The system can collect and convert the solar energy into chemical form by yielding useful chemical products. The environment-friendly PEC technology is considered as one of the most promising routes for sustainable development. In the water splitting case, green fuel hydrogen can be produced from water under irradiation. The sunlight is harvested by n-type and p-type semiconductor absorbers (see section 1.3) which act as photoanode and photocathode, respectively.⁹ In the PEC cell, the photoanode and/or photocathode, which are immersed in suitable electrolyte, are connected through an external circuit to a counter electrode, see Figure 1.2.1.⁹ When a
semiconductor electrode is immersed in contact with an electrolyte, a space-charge layer forms on each side of the semiconductor/electrolyte interface junction. The space-charge layer induces an electric field, which is one critical factor for charge separation. The charge distribution differs from the bulk materials in the region of space-charge layer. These originate from the semiconductor Fermi level equilibrating with the redox potential of electrolyte solution because of electron transfer between the semiconductor and the electrolyte solution. On the electrolyte side, the compact (Helmholtz) layer forms at the interface and extends to the bulk liquid with the diffuse (Gouy-Chapman) layer in between. On the photoelectrode side of the junction band bending occurs which depends on the position of the Fermi level. When the photoelectrodes are irradiated, electrons and holes are generated if the semiconductor absorbs photons with higher energies than its band gap. In the n-type semiconductor photoanode case presented in Figure 1.2.1a, water is oxidized to oxygen by the accumulated photoexcited holes on the surface of the semiconductor. Meanwhile, water is reduced to hydrogen on the counter electrode by electrons which are transferred from the photoanode back contact via an external circuit. In order to generate oxygen, the top of the valence band of the n-type semiconductor must be more positive than the oxygen evolution potential. In the p-type photocathode case presented in Figure 1.2.1b, the bottom conduction band position has to be more negative than the hydrogen evolution potential to produce hydrogen. The PEC reactions on photoelectrodes for the above two cases are driven by photogenerated minority carriers. In most case, an external bias must be supplied to yield PEC reactions via efficient charge separation. The tandem PEC system presented in Figure 1.2.1c consists of a n-type photoanode connected with an appropriate p-type.

![Energy diagrams of PEC cell using (a) a photoanode, (b) photocathode, and (c) photoanode and photocathode in tandem configuration.](image)

**Figure 1.2.1** Energy diagrams of PEC cell using (a) a photoanode, (b) photocathode, and (c) photoanode and photocathode in tandem configuration.

### 1.3 Photoelectrode Materials

#### 1.3.1 Fundamentals of Semiconductors

Semiconductors are the basic materials which absorb sunlight to obtain energy to split water into hydrogen and oxygen. Comparing with conductors and insulators, semiconductors
have intermediate electric conductivity which is related to the energy band.\textsuperscript{12} The crystal structure of semiconductors consist of repetitive three-dimensional translation unit cells, the smallest grouping of atoms. When the atomic orbitals overlap with each other, the crystallographic orbitals will be so closely spaced in energy that they are considered to form a continuum of electronic states, also known as energy band.\textsuperscript{12} In the energy band of a semiconductor, a series of bands are fully filled with electrons, the highest energy band containing the electrons is denoted as the valence band (VB). The bottom of the empty bands, which is closest to the valence band in energy, is the conduction band (CB). The former one is a measure of the ionization potential, of the bulk material. The latter one is a measure of the electron affinity, of the compound.\textsuperscript{13} There is a “gap” located between VB and CB, defined as band gap ($E_g$), where no electronic states exist. Figure 1.3.1 depicts the electronic structures of insulators, semiconductors and electric conductors. In semiconductors, the band gap is small enough so that sufficient energy can move a small fraction of the electrons from the valence band into the conduction band. The excitation of electrons makes a semiconductor conductive.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure131.png}
\caption{The illustration band gap of insulator, semiconductor and conductor.}
\end{figure}

The Fermi energy, $E_F$, represents the electron chemical potential in a semiconductor.\textsuperscript{13} $E_F$ is important to understand the electric and thermal properties of semiconductors. In intrinsic semiconductors, $E_F$ is essentially halfway between the valence and conduction bands, see Figure 1.3.1 center. On the contrary, the “extrinsic semiconductor” can be obtained by doping insulating materials and intrinsic semiconductors.\textsuperscript{14} A small amount of dopant impurity can affect the energy bands. The n-type and p-type semiconductors are the two kinds of extrinsic semiconductors resulting from intentional doping. In extrinsic semiconductors, additional energy levels are added by the impurities. The diagrams of n-type and p-type semiconductors band energy are depicted in Figure 1.3.2.
The band of n-type and p-type semiconductors with extra energy levels.

The distinction between direct and indirect semiconductors is another semiconductor property regarding to the nature of the optical transition between the valence and conduction bands. For direct semiconductors, the top valence band and the bottom conduction band have the same value of electron momentum, as shown in Figure 1.3.3. When the top valence band lies at a different value of electron momentum to the bottom of the conduction band, the semiconductor is indirect. The absorption coefficient of indirect semiconductors is much smaller than that of direct semiconductors because the indirect transitions require absorption or emission of a phonon carrying very little momentum. Electrical conductivity of semiconductors is associated with the number of mobile charge carriers. When the semiconductors are used as photoelectrodes, the high electrical conductivity facilitates charge transport in the semiconducting materials. Additionally, the electrical conductivity depends on the number of carriers or carrier density and electron mobility. A superior charge transport is expecting for higher carrier density and electron mobility. The intrinsic defects or the presence of impurities can induce a higher charge carrier concentration.

The illustration the direct band gap (a) and indirect band gap (b) in the E-k space between the valence and conduction bands. The indirect transition requires the assistance of extra phonon energy.
The semiconductor/electrolyte junction interface significantly affects the PEC reaction process. In the semiconductor, the Fermi level potential corresponds to the chemical potential of electrons. In the electrolyte, the redox potential of the redox couples represents the Fermi level of the electrolyte or the electrochemical potential of electrons. For a n-type semiconductor, the Fermi level is usually higher than the redox potential of an aqueous electrolyte. When a n-type semiconductor is immersed in an electrolyte forming a semiconductor/electrolyte junction, electrons flow to the electrolyte across the junction until the semiconductor Fermi level and the potential of the electrolyte redox couple are equilibrated. For a p-type semiconductor, the Fermi level is lower than that of the electrolyte, and the electrons transfer from the electrolyte to the semiconductor during the formation of semiconductor/electrolyte junction. In case of n-type semiconductor, after the equilibrium positive charges accumulate in the depletion region. The region, which is formed near the semiconductor surface due the moving away of electrons, is called space charge region (SCR). The SCR thickness usually ranges from 100 Å to several microns depending on the conductivity of the semiconductor and the amount of band bending. The charge distribution in SCR differs from the charge distribution in the bulk semiconductor. On the electrolyte side of the junction, negative charged ions are accumulated to balance the positive charges in the SCR forming a compact (Helmholtz) layer followed by a diffusion (Gouy-Chapman) layer, as shown in Figure 1.3. The thickness of the Helmholtz layer is typically on the order of 1 Å. The charge distribution difference induces upward bending of the conduction and valence band edges of the semiconductor. In addition, a potential barrier is established against further electron transfer from the semiconductor into the electrolyte through the junction. The reverse would be the case for a p-type semiconductor, and the band edges of the semiconductor are bent downwards. There is a potential at which no charge transfer and no band bending, the potential is called flat band potential ($E_{fb}$). At the $E_{fb}$, the Fermi level of the semiconductor is equal to the redox potential of the electrolyte. The flat band potential is a critical parameter which connects the energy levels of the electrolyte and the semiconductor. The flat band potential $E_{fb}$ is a very useful quantity in photoelectrochemistry as it defines the transition between depletion and accumulation effects and thereby is associated with the energy of the band edge of a given semiconductor material. The semiconductor bands are flat i.e. zero space charge in the semiconductor at the flat band potential. It is generally measured with respect to a reference electrode, because the potential difference between the sample being measured and the reference electrode can be estimated using the Equation 1.3.1:

$$E_{fb}(\text{NHE})=(\chi+\Delta E_f-V_H)-4.5 \text{ (eV)}$$  \hspace{1cm} 1.3.1

where $\chi$ is the electron affinity of the semiconductor, $\Delta E_f$ is the difference between the Fermi level and the majority charge carrier band, $V_H$ is the potential drop across the Helmholtz layer,
and 4.5 is the difference relating the H⁺/H₂ redox level to vacuum. It can be seen that the flat band potential is directly related to the the intrinsic properties of the semiconductor and the electrolyte, indicating a property of the interface. The flat band potential can be experimentally determined using the Mott-Schottky equation:

\[
\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 A^2 e N_D} (E - E_{fb} - \frac{k_B T}{e})
\]

where \(C\) and \(A\) are the interfacial capacitance and area, \(\varepsilon\) and \(\varepsilon_0\) are the dielectric constant and the permittivity of vacuum, \(e\) is the electronic charge, \(E\) is applied voltage, \(k_B\) and \(T\) are Boltzmann’s constant and the absolute temperature, \(N_D\) is the number of donors. Therefore, a plot of \(1/C^2\) against \(E\) should yield a straight line from which \(E_{fb}\) can be determined from the intercept on the V axis.

![Energy diagrams of n-type semiconductor/electrolyte junction interface.](image)

**Figure 1.3.4** Energy diagrams of n-type semiconductor/electrolyte junction interface.

### 1.3.2 Photoelectrode Materials

Over the past 40 years, the PEC technology has received increasing attention since the first report of TiO₂ photoanode in 1972. However, the practical applications remain a scientific challenge because of complex material prerequisites, which have to be matched simultaneously. The development of stable and efficient photoelectrodes is the major issue that hinders PEC application severely. There are critical and basic prerequisites in searching semiconductor materials to design PEC cells. First of all, the band gap required for the semiconductor is 1.23 eV without considering the overpotential on both hydrogen and oxygen evolution reactions; the band gap should have the capability to absorb the visible light which represents the significant segment of the solar spectrum (see 1.3.5). Thus, a band gap value between 1.6 eV and 3.2 eV is expected. Simultaneously, the valence and conduction band edge have to be higher than the HER potential and lower than the oxygen evolution reaction (OER) potential, respectively. Secondly, the economic factors have to be considered in order to apply PEC technology globally. Therefore, the elements used for PEC cell have to be the inexpensive, earth abundant and non-toxic. The third important criterion
for designing PEC cells is that the semiconductors need to be stable under the specific operation conditions. The high minority and majority carrier conductivities and fast surface kinetics properties of the semiconductors are also important factors to achieve a higher solar-to-hydrogen conversion efficiency. Up to date, no single material investigated so far fulfills all of the requirements.

Figure 1.3.5 ASTM G173-03 standard tables for reference solar spectral irradiances.

1.4 Strategies for Boosting Efficiency

The PEC water splitting performance of semiconductors is restrained by several factors, such as slow kinetics of surface reactions, rapid photogenerated charges recombination, photocorrosion and so on. A series of modification strategies, including doping, controlling morphology, loading catalysts and constructing heterojunctions etc. have been explored. Considering the limited success of the single strategy, multiple methods have to be used simultaneously to further enhance the efficiency of photoelectrodes. Several main approaches to improve PEC efficiencies are discussed below.

Doping

A way to increase the light absorption of semiconductors, is by introducing a foreign element into the crystal structure of semiconductors. Doping heteroatoms into the bulk semiconductors can form donor levels or acceptor levels and change the position of the Fermi level, thus significantly affecting the intrinsic optical property. The narrowed band gap could shift the absorption edge towards bathochromic, that’s more visible light photons can be absorbed by doped semiconductors. For example, the most common photoactive TiO$_2$ in UV region has been doped resulting a visible light absorption edge by numerous reports. For example, the photoconversion efficiency of TiO$_2$ has been increased by doping with boron element.

Besides absorption edge, doping also can adjust the semiconductors’ electrical resistivity which is related to the carrier transport properties and carrier concentrations. Cava
and Bocarsly et al. have investigated insights into the fundamental carrier transport properties and the effect on the PEC water splitting performance on model of a CuIn(S$_{1-x}$Se$_x$)$_2$ (0 ≤ x ≤ 1) chalcopyrite semiconductor. The results show that a low Mg doped concentration induce a four-order magnitude decrease in bulk electrical resistivity and a higher majority carrier concentrations.

**Crystal Facet Engineering**

The fundamental physical and chemical properties of semiconductors can be tuned via crystallographic orientation and exposed facet control. The charge separation efficiency plays a crucial role on the performance of PEC water splitting. A controlled semiconductor crystallographic orientation allows to expose favorable surface and surface atomic structure which induce preferential sites for PEC water splitting. The better charge transport properties generally cause promoted charge separation. These have been demonstrated by researchers on several materials, such as BiVO$_4$, Fe$_2$O$_3$ and Cu$_2$O. Cho and Zheng et al. have successfully deposited a BiVO$_4$ thin film photoanode with a preferred [001] growth orientation and exposed (001) facets. The preferentially [001]-oriented BiVO$_4$ exhibited an impressive photocurrent density, which is approximately 16 times higher than that exhibited by the randomly oriented BiVO$_4$ photoanode. The enhanced performance was proved to stem from excellent intrinsic charge transport properties and surface reactivity of preferentially [001]-oriented BiVO$_4$.

**Structure Engineering**

Some key properties of semiconductors can be tuned via morphology design and engineering. In addition to the intrinsic properties of semiconductors, the PEC properties are also sensitive to extrinsic factors such as difference in contact area with electrolyte and density of grain boundaries. Textured, nanosized or branched structures could not only reduce reflectance, i.e. improving light absorption, but also provide high surface area offering active sites. Superior PEC reaction activities can be thus achieved since the reaction mainly occurs at the electrolyte-semiconductor interface. Nanostructures such as nanowires and nanoflakes can shorten the charge transport distances to the electrolyte-semiconductor interface while maintaining a long optical pathlength for high absorption, resulting in higher charge separation efficiency and thus promoting PEC reactions than the flat dense film.

**Cocatalyst**

Another well-recognized approach is to integrate electrocatalysts on the semiconductor photoelectrodes. The loaded catalytic materials can accelerate and regulate the surface reaction kinetics. The cocatalyst on the semiconductor surface provides additional reaction sites, promoting the photoinduced charges separation and the interfacial charge transferring. The activation energy required for the hydrogen or oxygen evolution reactions
can be lowered, indicating a smaller overpotentials. In addition, specific functional layers can inhibit side or back reactions and protect the semiconductor from corrosion, increasing the lifetime of the photoelectrodes. The noble metal platinum is one of the best catalysts for HER due to the ideal bonding strength to H making it easily both to adsorb and reduce H\(^+\), as well as to release \(\text{H}_2\) afterwards. Gray and Lewis have modified the p-type WSe\(_2\) photocathode with a Pt cocatalyst to obtain a significant cathodic. For n-type semiconductor photoanodes, extensive studies have been carried out to exploit the adequate cocatalysts for OER.

1.5 Dissertation Overview

This thesis will be divided into 6 main chapters, starting with this section an introduction on PEC technology for hydrogen production, together with the fundamental of PEC and semiconductors, and the bottleneck of PEC technological problems.

Chapter 2 covers the results and discussions of the CuWO\(_4\) photoanode for PEC water oxidation which has been improved by post-treatment under oxygen-scarce atmosphere.

Chapter 3 covers the results and discussions of the quaternary nanowire thin film SrTaO\(_2\)N photoanode which has been used to construct a core-shell structure yielding an hole extraction gradient to improve the performance impressively.

Chapter 4 covers the results and discussions of the particle-based thin film CaTaO\(_2\)N photoanode which has been improved by acidic etching, and the origins in photocurrent has been investigated by different techniques including solid-state nuclear magnetic resonance.

Chapter 5 covers the results and discussions of the mössbauerite as an iron-only cocatalyst to improve the PEC OER performance by coupling with WO\(_3\) photoanode.

Chapter 6 covers the results and discussions of a p-WSe\(_2\) single-crystal photocathode which has been modified with monodisperse FePt and Pt nanocrystals as HER cocatalysts. The chemical bonding and water adsorption on the nanocrystals at the density functional theory (DFT) level has been analyzed to understand different electrochemical activities.

Chapter 7 draws a conclusion on the whole thesis and possible future work has been proposed.

1.6 Experimental Characterization

The general measurement methods are listed below.

**Powder X-ray Diffraction**

Powder X-ray Diffraction (PXRD) patterns were recorded in the transmission mode on a STOE STADI-P diffractometer (Cu K\(\alpha_1\) radiation) equipped with a DECTRIS Mythen 1K detector.
**Scanning Electron Microscopy**

Scanning Electron Microscopy (SEM) were performed to observe the morphologies of the prepared materials or the thickness of the thin film. SEM images were acquired on a Leo Supra 35VP SMT (Zeiss).

**Ultraviolet-Visible Spectroscopy**

Ultraviolet-Visible (UV-Vis) spectra were collected on a Shimadzu UV-2600 spectrophotometer by using BaSO$_4$ as reference. Tauc plots were calculated for determination of the band gap with the Kubelka-Munk function $F(R) = (1 - R)^2/2R$, where R is the reflectance.

**X-ray Photoelectron Spectroscopy**

A Prevac photoelectron spectrometer equipped with a hemispherical analyzer (VG SCIENTA R3000) and a low-energy flood gun (FS40A-PS) was employed to determine the surface composition of the samples. The X-ray photoelectron spectra (XPS) were recorded using a monochromatized Al K$_\alpha$ ($E = 1486.6$ eV) aluminum source. The binding energies were referenced to the C 1s core level ($E_b = 284.6$ eV). The fitting of high-resolution spectra was obtained through Casa XPS software.

**(Photo)electrochemical Measurements**

The simulated visible light (AM 1.5G, 100 mW cm$^{-2}$) source in the thesis was generated by a solar light simulator (class-AAA 94023A, Newport) equipped with an ozone-free 450 W xenon short-arc lamp. All PEC measurements including electrochemical impedance spectroscopy (EIS) and Mott-Schottky were carried out in a PEC cell (WAT Venture) which was operated in the conventional three-electrode system under illumination or dark condition. The thin film photoelectrode was used working electrode. A platinum wire and a 1 M Ag/AgCl electrode were used as counter electrode and reference electrode, respectively. A SP-150 (BioLogic), PalmSens4 (PalmSens BV) or INTERFACE 1010T (Gamry) were used to recorded electrochemical data. All current values were recorded versus 1 M Ag/AgCl and converted to versus reversible hydrogen electrode (RHE) according to Nernst equation ($E_{\text{RHE}} = E_{1M \text{Ag/AgCl}} + 0.059 \times \text{pH} + E_{\text{Ag/AgCl}}$). Linear sweep voltammetry (LSV) was swept with a scan rate of 10 mV s$^{-1}$ toward the positive (photoanode) or negative (photocathode, i.e. WSe$_2$ in chapter 6) direction at different potential ranges. Mott-Schottky measurements were performed in a dark setting at ac amplitude of 5 mV or 10 mV and at different frequencies. EIS was measured at different potential in an ac potential frequency range.

In chapter 2, the incident photon to converted electron (IPCE) was determined by using monochromatic light which was generated by a 300 W arc xenon light source. The light intensity at the chosen wavelength was determined with an UV-enhanced silicon
photodetector (818-UV, Newport) from 380 to 650 nm. The IPCE was calculated according to
IPCE (%) = (I × 1240 V nm)/(λ × P) × 100; where I is the photocurrent density (mA cm\(^{-2}\)), \( \lambda \) is
the measured wavelength (nm), and \( P \) is the intensity of incident light (mW cm\(^{-2}\)).

Different electrolytes were used for different photoelectrodes according to their
properties. In order to determine charge separation efficiencies of CuWO\(_4\) (chapter 2), a hole
scavenger Na\(_2\)SO\(_3\) was added into the electrolyte.
2 Augmenting the Photocurrent of CuWO₄ Photoanodes by Heat Treatment in the Nitrogen Atmosphere

2.1 Introduction

![Crystal Structure of CuWO₄](image)

*Figure 2.1.1* The crystal structure of CuWO₄. Tungsten, copper and oxygen atoms are drawn in red, green and blue, respectively. CuO₆ elongated octahedrons are drawn in cyan.

The high stability in neutral electrolytes and low costs make semiconducting oxides encouraging photoanode candidates.⁴¹ The ternary oxide CuWO₄ is one typical example for PEC water oxidation in neutral electrolytes due to a band gap of 2.2–2.4 eV. Previously reports reveal that CuWO₄ crystallizes in a distorted wolframite-type structure⁴², as depicted in Figure 2.1.1. The structure is triclinic, with space group Pī. Both the Cu²⁺ (3d⁹) and W⁶⁺ (5d⁰) cations are surrounded by O²⁻ ions (O 2p⁶), constructing distorted octahedrons due to the Jahn-Teller effect in Cu²⁺. In ternary CuWO₄, a secondary Cu²⁺ cation is added comparing to the binary WO₃.⁴³ There is a strongly hybridized state of Cu 3d-O 2p contributing to the top of the valence position of CuWO₄ because the energy level of the Cu 3d orbitals is close to that of O 2p. The band gap of CuWO₄ is reduced comparing to WO₃ because its conduction band is mainly composed of W (5d) orbitals, as displayed in Figure 2.1.2.

Theoretically, CuWO₄ can achieve a greater photocurrent density than the currently best-performing vanadium-based oxide BiVO₄⁴⁴ owing to a narrower band gap by 0.2 eV.⁴⁵ Researchers have been fabricated CuWO₄ photoanode with different morphologies such as dense thin films,⁴⁶ porous meshes,⁴⁷ nanoflakes,⁴⁸ and related anisotropic shapes⁴⁹ to improve its performance. Different dopants such as molybdenum,⁵⁰ zinc,⁵¹ and iron⁵² also have been used to modify CuWO₄ in order to achieve larger photocurrent.²² Functionalizing
the CuWO₄ photoanode surface with noble metal such as silver nanowires⁵³ and gold nanoparticles⁵⁴, or manganese-based cocatalysts⁵⁵ also can enhance water oxidation, building a heterojunction with other semiconductor is also an approach.⁵⁶ The Ag₂NCN overlayer has been demonstrated the suppressing of charge-carrier recombination.⁵⁷ It should be noted that the overlayers have to be thin to enable an efficient surface reaction.⁵⁸

**Figure 2.1.2** The band gap diagrams of WO₃ and CuWO₄.

The preparation procedures significantly affect the CuWO₄ photoelectrodes surface properties, even with the same morphology.⁵⁹ The surface properties of inorganic materials are known generally sensitive to the environment.⁶⁰ Recently, an efficient route to modulate the photoelectrodes surface properties by post-treatment under different atmospheres, such as hydrogen, oxygen, argon, and nitrogen has caught a lot attention.⁶¹ Such post-treatment could incorporate the atmosphere elements into the materials and/or regulate the oxygen vacancies numbers.⁶² The oxygen vacancies may induce new active reaction sites with sophisticated adsorption energy for H₂O molecules on the photoelectrode surface.⁶³

For instance, the photocurrent of α-Fe₂O₃ is heavily influenced by different oxygen vacancy concentrations, whereas the onset potential can be turned up to 0.2 V negatively.⁶⁴ A nitrogen incorporated into BiVO₄ thin film photoanode has been reported by Choi et al. via post-annealing at relatively low temperatures. The post-treatment induced a narrow band gap and superior light absorption.⁶⁵ An enhanced photocurrent and bathochromic shift of the ultraviolet-visible absorption spectra were achieved over CuWO₄ thin-film photoanodes after post-annealing under hydrogen atmosphere.⁶⁶ In this chapter, the thin-film CuWO₄ was synthesized on fluorine-doped tin oxide (FTO) glass by means of electrodeposition. The post-annealing effect under nitrogen atmosphere was investigated. The amplified performance of the thin films over PEC water oxidation were discussed combing UV-Vis spectroscopy and EIS.
2.2 Experiments

2.2.1 Synthesis of CuWO₄ Photoanodes

A modified route by Bartlett et al. was used to synthesize CuWO₄ thin films on FTO glass slides (2.2 mm thick, Sigma-Aldrich). The FTO glass slides were cleaned before use by sonication in diluted hydrochloric acid (Sigma) and ethanol for 20 min. The electrolyte solution of pH 1 containing Cu and W cations was used for electrodeposition of the copper-tungsten matrix. In order to prepare the electrolyte, 15 mL of deionized water and 2.5 mL of hydrogen peroxide (30%, Geyer Chemsolute) mixture solution were used to dissolve 1.73 g sodium tungstate dihydrate (Na₂WO₄·2H₂O, 5.2 mmol, 99.9%, Acros Organics) under stirring with magnetic bar. Additional deionized water (25 mL) and 22.5 mL of isopropanol (>99.7%, SigmaAldrich) were added to the above solution. The Cu precursor solution was prepared by dissolving 0.73 g copper(II) nitrate trihydrate [Cu(NO₃)₂·3H₂O, >99%, Sigma] in 10 mL deionized water. Then the Cu precursor solution was added to the W precursor solution, and the pH value of mixture solution was adjusted to 1 slowly by adding an appropriate amount of diluted nitric acid (Sigma-Aldrich). The mixture solution was stirred for 10 mins before electrodeposition in three electrodes system. A pre-cleaned FTO glass, a platinum wire and 1 M Ag/AgCl were served as working electrode, counter electrode and reference electrode respectively. For electrodeposition, cyclic voltammetry technique was swept in the potential range from −0.5 to + 0.5 V versus 1 M Ag/AgCl reference electrode for 12 cycles at a scan rate of 50 mV s⁻¹. After the electrodeposition process, the FTO glass was removed from the electrolyte, washed with deionized water and dried under vacuum. Then the FTO glass with copper-tungsten matrix was annealed at 773 K for 2h under ambient atmosphere to obtain CuWO₄. After cooling down to room temperature naturally, etching in 0.5 M HCl for 20 min was carried out to remove excess of copper oxide to get pure CuWO₄. The modified CuWO₄(N) was obtained by post-annealing the PEC-measured and washed CuWO₄ under an oxygen deficient atmosphere, i.e. nitrogen flow at different temperatures for 3.5 h.

2.3 Results and Discussion

2.3.1 Structural Characterization

In order to avoid the reflections of tin oxide on the FTO glass, a small area of the thin film was mechanically removed from the FTO substrate to carry out PXRD measurement. Figure 2.3.1 shows the PXRD patterns of pristine CuWO₄ thin films and post-annealed CuWO₄(N) in a nitrogen atmosphere at 623 K. Comparing with the CuWO₄ simulated patterns, it can be seen the material is pure and single phase. Furthermore, the CuWO₄(N), which was post-annealed under a nitrogen atmosphere at 623 K for 3.5 h similarly to the modified thin films of BiVO₄, does not show any impurity phase peaks.
Figure 2.3.1 Experimental and simulated PXRD patterns of CuWO$_4$ and CuWO$_4$(N) thin films.

Figure 2.3.2 XP spectra of nitrogen for CuWO$_4$ and CuWO$_4$(N).

XPS was performed to detect the surface copper, tungsten, and nitrogen concentration changes before and after nitrogen treatment. Figure 2.3.2 displays the XP spectra of nitrogen for CuWO$_4$ and CuWO$_4$(N). No N 1s signal was detected in the spectra, indicating the CuWO$_4$ structure was not incorporated with notable amount of nitrogen element during post-annealing under N$_2$ flow. Figure 2.3.3 shows the high resolution XP spectra of W 4f at the selected regions. No notable difference was observed in the core level W 4f XP spectra between pristine CuWO$_4$ and N$_2$-treated CuWO$_4$(N) thin films. The phenomenon is contrast to the previous reports on H$_2$-treated CuWO$_4$ thin films. In the H$_2$-treated CuWO$_4$ thin films case, the core level W 4f shifted clearly to the lower binding
energies, indicating a partial reduction of W\textsuperscript{6+} to W\textsuperscript{5+} because of the high reduction atmosphere of H\textsubscript{2}.\textsuperscript{67}

![Figure 2.3.3](image1.png) XP spectra of W 4f for CuWO\textsubscript{4} and CuWO\textsubscript{4}(N).

![Figure 2.3.4](image2.png) XP spectra of Cu 2p for CuWO\textsubscript{4} and CuWO\textsubscript{4}(N).

A doublet at 34.9 eV (W 4f\textsubscript{7/2}) and 37.1 eV (W 4f\textsubscript{5/2}) as well as a loss feature above 40 eV were observed obviously, implying that W maintained as W\textsuperscript{6+} upon nitrogen post-annealing. In the spectrum of Cu 2p (Figure 2.3.4), in case of pristine CuWO\textsubscript{4} the peaks center of Cu 2p\textsubscript{3/2} and Cu 2p\textsubscript{1/2} lied at 933.5 and 953.4 eV. While in case of CuWO\textsubscript{4}(N) the peaks center of Cu 2p\textsubscript{3/2} and Cu 2p\textsubscript{1/2} shifted to higher binding energies of 933.9 and 953.9 eV, respectively. Furthermore, the spectrum of the two samples exhibit satellites with the same shape, typical of Cu\textsuperscript{2+}. The discussed characteristics are similar to those previously reported on CuWO\textsubscript{4}.\textsuperscript{66–71}
upon post-treatment under nitrogen, at a slightly higher temperature of 673 K, was previously reported for the superconducting oxide YBa$_2$Cu$_3$O$_{7-x}$.	extsuperscript{72} When annealing under a nitrogen atmosphere at 1073 K, the authors observed subsequently a shift of the copper cation signal toward smaller binding energies, similar to H$_2$-treated CuWO$_4$ thin films.

![](image)

**Figure 2.3.5** Tauc plots for CuWO$_4$ and CuWO$_4$(N) photoanodes. The dashed lines represent the extrapolation for the determination of the band gap.

The UV-Vis spectroscopy was employed to determine the electronic band gaps of CuWO$_4$ and CuWO$_4$(N). Figure 2.3.5 depicts the corresponding Tauc plots for an indirect transition, an almost identical band gap of 2.45 eV for CuWO$_4$ and CuWO$_4$(N) can be determined. This is agreed with the lack of N element incorporation into the CuWO$_4$ crystal structure upon nitrogen treatment at 623 K. In contrast with CuWO$_4$, nitrogen treatment of BiVO$_4$ under the same conditions can lead to a bathochromic effect of around 0.2 eV because of nitrogen incorporation.

### 2.3.2 Photoelectrochemical Water Oxidation

LSV curves were first carried out to analyze the CuWO$_4$ and CuWO$_4$(N) photoanodes in the KP$_1$ electrolyte at pH 7 under sequentially chopped AM 1.5G illumination (Figure 2.3.6). It should be pointed out that the same photoanode was used to perform all PEC measurements for comparison between CuWO$_4$ and CuWO$_4$(N). The photocurrent of pristine CuWO$_4$ and N$_2$-treated CuWO$_4$(N) photoanode both expose a significant upsurge at around 0.8 V versus RHE, the current was driven by the photogenerated charges. When chopping the illumination, an abrupt current drop was observed. The N$_2$-treated CuWO$_4$(N) photoanode establishes a meaningfully superior photocurrent than that of the pristine CuWO$_4$ electrode, and some small spikes in the current density were observed over illuminating. From the
chronoamperometry (CA) curves at 1.23 V versus RHE, the spikes are also noticeable (Figure 2.3.7).

As shown in Figure 2.3.7, the CuWO$_4$ (N) photoanode develops a photocurrent settling at 80 μA cm$^{-2}$, whereas the pristine CuWO$_4$ photoelectrode only produces a much lower photocurrent of 30 μA cm$^{-2}$. The IPCE curves of CuWO$_4$ before and after nitrogen treatment at 1.23 V versus RHE under AM 1.5G illumination are shown in Figure 2.3.8, a similar trend
can be found. It can be seen that the photocurrent onset generates at the same wavelength of ca. 520 nm, which is consistent with the UV-Vis absorption data.

Figure 2.3.8 IPCE of CuWO$_4$ and CuWO$_4$(N) photoanodes in pH 7 0.1 M KP$_i$ electrolyte at 1.23 V versus RHE under backlight AM 1.5G illumination.

A separate CuWO$_4$ electrode, which was heated at the identical temperature and period but under an ambient atmosphere rather than N$_2$, was measured for comparison. The CuWO$_4$ thin film electrode was rinsed with deionized water to wipe the electrolyte from the surface before annealing. As shown in Figure 2.3.9, the photocurrent decreased after
annealing under an ambient atmosphere. The result designates that annealing under an oxygen-deficient atmosphere is vital to improve the CuWO$_4$ performance.

![Figure 2.3.10 LSV of CuWO$_4$ annealed at different temperatures under nitrogen in pH 7 0.1 M KP$_i$ electrolyte at a scan rate of 10 mV s$^{-1}$ under chopped backlight AM 1.5G illumination.](image)

To determine the dependency of the annealing temperature under nitrogen on the photoelectrode performance, a series of CuWO$_4$ photoanodes was fabricated. The corresponding LSV curves are summarized in Figure 2.3.10, it can be seen that the electrode annealed under nitrogen at 623 K develops the highest photocurrent density. After the annealing temperature under nitrogen exceeding 623 K, lower photocurrent was obtained. The reasons are likely to be sintering results and the simultaneous loss of surface area. Additionally, the XP spectra of the electrode annealed at 773 K under nitrogen does not present noticeable amounts of nitrogen (Figure 2.3.11).

![Figure 2.3.11 XP spectra of nitrogen for CuWO$_4$ photoanode annealed at 773 K under nitrogen.](image)
The charge separation efficiencies $\eta_{\text{sep}}$ of CuWO$_4$ photoanode before and after nitrogen treatment were calculated to identify whether post-annealing under nitrogen can lead to a higher concentration of photogenerated holes on the electrode surface. Due to the relative slow kinetics of water oxidation, a hole scavenger in the form of 0.1 M sodium sulfite was used to accelerate the PEC oxidation process as a function of the applied potential a function of the applied potential. Thus, it’s able to determine the maximal photocurrent ($J_{\text{sulfite}}$) owing to almost all holes on the surface being consumed for oxidative processes. With the maximal photocurrent ($J_{\text{sulfite}}$), the charge separation efficiency can be estimated according to the formula:

$$\eta_{\text{sep}} = J_{\text{sulfite}} / (J_{\text{max}} \times \eta_{\text{abs}})$$

where $J_{\text{max}}$ is the theoretical maximum photocurrent of CuWO$_4$ equal to 10.7 mA cm$^{-2}$ and $\eta_{\text{abs}}$ is the absorption efficiency. The absorption efficiency $\eta_{\text{abs}}$ can be calculated by the integration of the product of the light-harvesting efficiency and incident spectral irradiance from 300 to 520 nm. The charge separation efficiencies as function of the applied potential were plotted in Figure 2.3.12. It should be noted that the $\eta_{\text{sep}}$ values of CuWO$_4$(N) are higher than that of CuWO$_4$, which manifests in the improved current density during water oxidation. In the bulk of material, the charge separation efficiency usually decreases because of recombination. The nitrogen treatment induced the higher values of $\eta_{\text{sep}}$, indicating enhanced transport properties of the charge carriers.

\[\text{Figure 2.3.12 Charge separation efficiencies } \eta_{\text{sep}} \text{ of CuWO}_4 \text{ and CuWO}_4(N) \text{ photoanodes.}\]

The extended light absorption can be expelled from the reasons for enhanced photocurrent because the band gaps of CuWO$_4$ and CuWO$_4$(N) are almost equal. Therefore, EIS measurements were carried out to investigate the origin of increased PEC performance of
the CuWO$_4$(N) photoanode. Figure 2.3.13 shows the typical Nyquist plots measured at 0.99 V versus RHE under AM 1.5G illumination.

![Figure 2.3.13](image)

Figure 2.3.13 Nyquist plots fitting for (a) CuWO$_4$ and (b) CuWO$_4$(N) measured at 0.99 V versus RHE under AM 1.5G illumination.

![Figure 2.3.14](image)

Figure 2.3.14 The equivalent circuit with two capacitive elements.

A simplified equivalent circuit shown in Figure 2.3.14 was used to simulate the recorded EIS data for CuWO$_4$ photoelectrodes. In the circuit, $R_s$ stands for the resistance from the bulk thin film, the electrolyte, and the electrical contacts. The bulk capacitance of the thin film and the resistance of trapped electrons at the surface are expressed as $C_{\text{bulk}}$ and $R_{\text{trap}}$, respectively. $C_{\text{ss}}$ and $R_{\text{ct,ss}}$ account for the surface-state capacitance and the charge-transfer resistance at the surface-electrolyte interface for water oxidation, respectively.

A typical simulated Nyquist plots of pristine CuWO$_4$ and N$_2$-treated CuWO$_4$(N) recorded at 0.99 V versus RHE under AM 1.5G illumination are shown in Figure 2.3.13. Two semicircles were exhibited for the pristine CuWO$_4$. In the N$_2$-treated CuWO$_4$(N) case, the semicircle is smaller than that of pristine CuWO$_4$, suggesting an improved charge-carrier conductivity for the CuWO$_4$(N) photoanode.

Figure 2.3.15 shows the Mott-Schottky plots for the CuWO$_4$ and CuWO$_4$(N) photoanodes under dark conditions. The charge-carrier density $N_d$ can be calculated from the Mott-Schottky plots according to the following formula:

$$N_d = \frac{2}{e_0 \varepsilon \varepsilon_0} \left( \frac{d(1/C^2)}{dV} \right)^{-1}$$  \hspace{1cm} 2.3.2
where $e_0$ is the electron charge equal to $1.6 \times 10^{-19}$ C, $\varepsilon$ is the dielectric constant for CuWO$_4$ equal to 83$^{67}$, $\varepsilon_0$ is the permittivity of vacuum equal to $8.85 \times 10^{-12}$ F m$^{-1}$, and $V$ is the applied potential. In this formula, capacitance was extracted from the EIS data at different applied potential under dark conditions. According to the linear regression of the Mott-Schottky plots the flat-band potentials were calculated. The pristine CuWO$_4$ has a flat-band potential at 0.44 V versus RHE and the CuWO$_4$(N) was estimated to have a slightly more negative flat-band potential of 0.42 V. In both cases, the values are akin to previous reports on CuWO$_4$ electrodes. A semiconducting n-type behavior was also confirmed by the positive slope of both the plots.

Figure 2.3.15 Mott-Schottky plots of CuWO$_4$ and CuWO$_4$(N) electrodes recorded at 484 Hz in the dark.

Figure 2.3.16 Mott-Schottky plots of (a) CuWO$_4$ and (b) CuWO$_4$(N) electrodes recorded at different frequencies under backlight AM 1.5 G illumination.

The N$_2$-treated CuWO$_4$(N) develops a reduced slope than the pristine CuWO$_4$, indicating an enriched electron donor density by more than 30% from $30.3 \times 10^{18}$ to $40.1 \times$
The high electron donor density boosts the electronic conductivity and profits the charge-carrier separation. It is acknowledged that the CuWO₄ performance for PEC water oxidation can be advanced by oxygen vacancies. The oxygen partial pressure during annealing affects the oxygen vacancy concentration. Thus, annealing in an oxygen-deficient atmosphere i.e. nitrogen would induce more oxygen vacancies for the CuWO₄ electrodes.

The frequency-dependent capacitances at smaller values (0.58, 1.6, and 11.9 Hz) under illumination for CuWO₄ and CuWO₄(N) were investigated, as shown in Figure 2.3.16. The slope changes with the frequency, whereas the flat band potentials are almost unaltered, indicating the Fermi level pinning due to a midgap state.

Upon illumination, the photoexcited electrons in the conduction band have three ways to go: diffusing through the FTO substrate to the cathode, recombining with holes, or diffusing to an intermediate surface state. While the holes can be used to oxidize water or become trapped in a midgap state. Figure 2.3.17 presents the four potential dependency of equivalent circuit elements of the circuit to model water oxidation for CuWO₄ photoanodes. The values changes of individual circuit elements follow the trend of potential-dependent as described previously by Bartlett. In case of the pristine CuWO₄
photoanode, the onset potential locates at 0.8 V versus RHE, whereas $R_{\text{ct,ss}}$ decreases at this potential. The $R_{\text{ct,ss}}$ shows an inverse relationship with photocurrent, indicating a larger potential could induce an improved charge transfer for water oxidation. Simultaneously, the upturn of $R_{\text{trap}}$ at 0.8 V versus RHE suggests the excited electrons in the conduction band are hindered to recombine with holes trapped in the midgap state. The $C_{\text{bulk}}$ show the relatively stable values, which is most likely associated with a persistent flow of photoexcited electrons from the bare CuWO$_4$ electrode toward the FTO substrate. The surface-state capacitance $C_{\text{ss}}$ starts increasing from 0.8 V versus RHE. The increasing of $C_{\text{ss}}$ has been proposed to be correlated with the hole transfer from the valence band to the midgap state as the rate-limiting process. The enhanced PEC performance of CuWO$_4$(N) photoanode is accompanied by a different potential dependency of the equivalent circuit elements. Contrary to the pristine CuWO$_4$, the $C_{\text{bulk}}$ value declines until 1.2 V versus RHE, where it stabilizes constantly. After post-treatment under nitrogen, the $R_{\text{trap}}$ drops from $7.1 \times 10^3$ Ω cm$^2$ at 0.8 V to $3.9 \times 10^2$ Ω cm$^2$ at 0.8 V versus RHE. Furthermore, the surface-state capacitance $C_{\text{ss}}$ falls from the beginning i.e. 0.8 V versus RHE, until it reaches a constant value at 1.14 V versus RHE.

A stronger shrink of the charge-transfer resistance $R_{\text{ct,ss}}$ of CuWO$_4$(N) is observed, inducing the improvement in photocurrent, comparing to the pristine CuWO$_4$ photoanode. In case of the post-treated CuWO$_4$(N) photoanode, $R_{\text{ct,ss}}$ falls from $5.0 \times 10^4$ Ω cm$^2$ at 0.84 V to $7.7 \times 10^3$ Ω cm$^2$ at 1.0 V versus RHE (Figure 2.3.17b). The PEC water oxidation could be promoted by photogenerated holes because of the reduce of charge-transfer resistance at the semiconductor-electrolyte interface. The formation of more oxygen vacancies may be the possible explanation for the reduction of $R_{\text{ct,ss}}$ upon nitrogen treatment. Thus, a higher amount and/or creation of new active sites for PEC water oxidation could be induced at the onset potential of 0.8 V versus RHE. In case of the related BiVO$_4$, the formation of oxygen vacancy modulated the surface properties by creating the vanadium site as the active site for PEC water oxidation.$^{63}$

### 2.4 Conclusions

In this chapter, annealing at 623 K in an oxygen-scarce atmosphere such as nitrogen has been demonstrated to be an effective route to augment PEC water oxidation performance of CuWO$_4$ photoanodes. After post-treatment under nitrogen atmosphere, the photocurrent increases from 30 to 80 μA cm$^{-2}$ at 1.23 V versus RHE under AM 1.5G illumination in a phosphate buffer electrolyte at pH 7. The alteration of charge carrier separation efficiency is correlated with the improvement in the photocurrent of CuWO$_4$ photoanode. N element is not incorporated into the crystal structure of CuWO$_4$ during the post-treatment, and the band gap remains almost the same. An identical post-annealing treatment under an ambient atmosphere instead of nitrogen did not augment the photocurrents.
Oxygen vacancies can be formed during the annealing in the oxygen-deficient atmosphere, the donor densities increase approximately 30%. The CuWO₄ and CuWO₄(N) anodes have comparable flat-band potentials of 0.44 and 0.42 V versus RHE, respectively. The EIS results indicate that the decrease of the charge-transfer resistance of the surface states is the reason of the augmented PEC efficiency of the CuWO₄(N) photoanode. In case of the pristine CuWO₄ photoanode, the decline in $R_{ct,ss}$ is substantially less profound and remains at a relatively constant value, which is similar to the resistance of trapped electrons at the surface. These results suggest that the post-annealing under nitrogen would induce an alteration of the mechanism for PEC water oxidation. The work in this chapter highlights the importance of post-annealing treatment of thin-film oxide semiconductors with respect to their surface properties for PEC water oxidation.
3 Quaternary Core-Shell Oxynitride Nanowire Photoanode Containing a Hole-Extraction Gradient for Photoelectrochemical Water Oxidation

3.1 Introduction

It is essential to develop a stable narrow band gap semiconducting material with capably utilizing visible light to obtain chemical fuel from solar energy. Besides extensively investigated n-type oxide-based semiconductors, such as ZnO, Fe₂O₃, and BiVO₄, several mixed anions (oxy)nitrides (e.g., Ta₃N₅, LaTiO₂N, BaTaO₂N, SrTaO₂N) with optical absorption edge above 550 nm have attracted considerable attentions. The suitable valence band edge and conduction band edge positions allow overall water splitting under bias-free conditions over these (oxy)nitrides. A narrow band gap of 2.3 eV endues SrTaO₂N a theoretical solar-to-hydrogen efficiency of 14.4%. The SrTaO₂N, which has tetragonally distorted perovskite structure with a space group of I₄/mcm (Figure 3.1.1), can be obtained via topotactic transformation from oxide precursor Sr₂Ta₂O₇. The Sr₂Ta₂O₇ possesses a layered perovskite structure which belongs to orthorhombic crystal system with a space group of Cmcm. The top of the valence band for the Sr₂Ta₂O₇ is built from O 2p orbitals, and the bottom of the conduction band mainly is composed of empty Ta 5d orbitals. When the O atoms of Sr₂Ta₂O₇ are fractionally replaced by N atoms, top of the valence band is shifted higher compared to Sr₂Ta₂O₇ due to the contribution of N 2p orbitals. After O 2p orbitals hybridized with electronegative N 2p, which only slightly affects the level of the bottom of
the conduction band, the band gap is reduced sufficient enough to respond to visible light (see Figure 3.1.2).\textsuperscript{84,85}

![Figure 3.1.2 Schematic band structures of oxide Sr\textsubscript{2}Ta\textsubscript{2}O\textsubscript{7} and oxynitride SrTaO\textsubscript{2}N.](image)

Aiming to advance the performance of oxynitride photoanodes, many methods have been explored.\textsuperscript{86} For oxynitride semiconductor materials, doping as well as nanostructuring\textsuperscript{87} has been demonstrated efficient in improving their photocatalytic performance, such as for Na-doped SrTaO\textsubscript{2}N\textsuperscript{82} and Ca-doped BaTaO\textsubscript{2}N\textsuperscript{88} photoanodes. Heterojunction also has been built based on oxynitride materials to achieve higher photocurrents.\textsuperscript{89} When the band edges are matched, the interfaces over the heterojunction would drive magnified charge-carrier separation.\textsuperscript{90} An example Sr\textsubscript{2}Ta\textsubscript{2}O\textsubscript{7-x}N\textsubscript{x}/SrTaO\textsubscript{2}N heterojunction has been designed and ameliorated the photocurrents of SrTaO\textsubscript{2}N electrodes.\textsuperscript{91} An metal-free C\textsubscript{3}N\textsubscript{4} semiconductor also has been used to construct heterojunction with TaON, deposition with CoO\textsubscript{x} nanoparticles would further improve the heterojunction performance.\textsuperscript{87} An cobalt-base layer on the photoanode is a general route to promote the water oxidation process.\textsuperscript{92}

An impeded charge-carrier separation is common over oxynitride thin films and their oxidic counterparts since the large electric resistance. The resistance can be reduced by annealing the oxynitride electrodes under an oxygen-deficient atmosphere.\textsuperscript{80} Another possibility to improve charge transport across agglomerated particle-based photoelectrode is post-necking treatment formatting a thin network layer connecting the particles.\textsuperscript{93}

The abovementioned methods are to try to overcome the three main problems related on PEC water oxidation: (i) the light-harvesting driven electron-hole pairs production, (ii) the separation and migration rather than the recombination of the photogenerated charges, and (iii) the reaction over surface triggered by the photogenerated charges.\textsuperscript{94} The other severe issue for oxynitrides photoelectrodes is the photocorrosion (i.e., the loss of nitrogen anions from the structure), which has to be controlled. The issue can be accomplished via deposition of a thin protective layer, such as Al\textsubscript{2}O\textsubscript{3},\textsuperscript{95} and TiO\textsubscript{2}\textsuperscript{x} on the semiconductor surface.
Different functional overlayers deposited on the photoelectrodes sequentially can improve the photoelectrode with respect to photocurrent and stability synergistically. An excellent Ta$_3$N$_5$ photoanode has been designed by Li et al., in which TiO$_x$ was used to decrease the electron-hole recombination and further coating with nickel hydroxide and ferrihydrite to store holes. The nanowire semiconductor thin film photoelectrodes manifest both high light harvesting and charge-carrier separation comparing with the flat electrodes. With respect to the one-dimensional structure, the short diffusion pathways facilitate the holes across the nanowire, and along the nanowire electrons are easy to be transferred to the counter electrode. Although a variety of synthesis methods have been used to prepare Ta$_3$N$_5$ and TaON photoelectrodes with one-dimensional structures, there is only one recent report on quaternary oxynitride nanowire photoanode such as SrTaO$_2$N.

In this chapter, a quaternary oxynitride nanowire photoanode has been prepared and deposited with different functional overlayers to yield a hole extraction gradient. In the core-shell structures, the photogenerated holes over the oxynitride core can be efficiently across the overlayers to the outer shell consisting of a catalyst for water oxidation. The obtained heterojunction photoanode is analyzed by several characterization techniques such as PXRD, XPS, transmission electron microscopy (TEM) and PEC.

### 3.2 Experiments

#### 3.2.1 Fabrication of SrTaO$_2$N Nanowire Thin Films

The Sr$_2$Ta$_2$O$_7$ precursor on tantalum substrate was synthesized by hydrothermal method and was then converted to SrTaO$_2$N by nitridation according to previous work. Prior to use, the tantalum foil (0.5 mm × 10 mm × 20 mm, 99.99 wt%, Smart Elements) was washed sequentially with diluted nitric acid, deionized water, and ethanol. 5.3 g of Sr(OH)$_2$·8H$_2$O (0.02 mol, 99.995 wt %, Sigma-Aldrich) was dissolved in 14 mL of Milli-Q water (18.3 Ω cm) in an autoclave, and after stirring tantalum foil was placed inside vertically. The mixture was bubbled with argon gas for 10 min before sealed and heated at 473 K for 20 hours. After cooling down to room temperature naturally, the tantalum foil was removed and washed with water, and dried. A white film was covered on the tantalum, and annealed at 923 K for 15 min. The white film was converted to oxynitride under flows of NH$_3$ (15 mL min$^{-1}$) and H$_2$ (5 mL min$^{-1}$) at 1273 K for 3 h. After nitridation, the sample was treated with 0.1 M HNO$_3$ solution for 20 s and washed with water.

#### 3.2.2 Deposition Overlayers on SrTaO$_2$N Photoanode

A modified electrodeposition route was used to deposit amorphous TiO$_x$ layer on SrTaO$_2$N nanowires photoanode. The deposition electrolyte was prepared by diluting 2 ml TiCl$_3$ (20%) in HCl (abcr GmbH) solution with 40 mL of deionized water and adjusted the pH
value to 2.45 ± 0.03 by dropwise addition of a 0.6 M NaHCO₃ solution. The deposition of TiOₓ layer was performed at 0.07 V versus 1 M Ag/AgCl for 15 s in a three electrodes system. After deposition, the SrTaO₂N/TiOₓ electrode was washed with water and dried under ambient atmosphere. The same deposition procedure but for 5 min was used to deposited on FTO glass.

A 25 mM NiSO₄ electrolyte at pH 6.9 (adjusted by adding NaOH) was used to deposited Ni(OH)ₓ layer at the potential of 1.17 V versus a 1 M Ag/AgCl electrode for 2 min.

The cobalt phosphate (CoPₓ) layer was deposited by a photo-assisted electrodeposition process. The deposition was conducted in an electrolyte containing 5 mM Co(NO₃)₂ and 0.1 M potassium phosphate (KPₓ) buffer at pH 7 at a constant potential of 0.2 V versus 1 M Ag/AgCl for 15 s under 1 sun (AM 1.5G) illumination.

3.2.3 Transmission Electron Microscopy

The electron energy-loss spectroscopy (EELS) and energy-dispersive X-ray spectroscopy (EDX) analysis depicted in Figure 3.3.5 was performed at 300 kV by means of a double-aberration-corrected Themis Z TEM fabricated by the FEI Company. Prior to measurement, the probe aberrations were corrected up to fourth order, and a probe current was 2 nA which yielded a usable spatial resolution of approximately 1.2 Å. The interest region was scanned by probe at a rate of approximately 400 nm/s, dwelling for just under 10 ms at each pixel position. The Velox 2.6 software (FEI Company) was used to acquire the EDX and the EELS signals simultaneously. A FEI Chemi-STEM detector in Super XG2 geometry was used to record the EDX spectra, while the EEL spectra were generated in the magnetic prism of a Quantum GIF 965 spectrometer (Gatan Inc). Both the low-loss and core-loss EELS regions could be simultaneously recorded because the spectrometer was equipped with dual-EELS capability. A 1 eV/channel of energy dispersion with an offset of 200 eV was employed for the core-loss region, enabling to capture all energy edges ranging from C-K at 284 eV to P-K at 2146 eV. The microscope electron optics were configured to use a convergence semiangle of 17.9 mrad and a collection semiangle of 30 mrad.

For data acquisition, the core-loss EELS data were handled by using multilinear single-value decomposition (MLSVD)⁹⁹–¹⁰¹ which was implemented in the TensorLab package for Matlab.¹⁰² The data was converted to approximately Gaussian noise space by weighting them prior to the decomposition¹⁰³ and centered about the mean observation. The maps in Figure 3.3.5 was produced by the data set which was generated by truncating the spectral mode of the MLSVD to the nine components of highest variance. The two spatial modes were left uncompressed. The reconstructed model was subtracted from the raw data, ensuring that the signal subspace was adequately approximated by the data compression, and an inspection of the scree plot and loading curves was used to estimate the rank of the reconstruction.

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The EELS analysis package in Digital Micrograph was used to generate the EELS maps in Figure 3.3.5. Hartree-Slater cross sections were fitted to the reconstructed core-loss data. The effects of plural scattering were corrected by fitting with the low-loss spectrum image. These offers quantitative inelastic scattering cross sections for thicknesses of up to approximately 1.4 mean free paths (corresponding to a total thickness of approximately 150 nm). The shell region localized P, Ni, and Co elements were observed in the EELS maps with weak evidence, as shown in Figure 3.3.4. However, it is unable to find the compelling evidence for the presence of these edges in the raw data. While it is possible that the maps reveal a slight change in the pre-edge background slope caused by the ionization edges under investigation. And this change was detected by MLSVD, the interpretation is somewhat ambiguous. Thus, more work would be needed to draw a conclusion.

In Figure 3.3.5, the absolute thickness is a calculated value derived from the ratio of elastic to inelastic scattering, which was captured in the low-loss EELS acquisition. These produce a thickness in units of the mean free path for the inelastic scattering of electrons with a kinetic energy of 300 keV. Due to the material-dependent of mean free path property, the average atomic mass at each pixel position extracted from the EELS maps was used to convert this to absolute thickness values.

3.3 Results and Discussion

3.3.1 Structural Characterization

![Graph showing PXRD patterns](image)

**Figure 3.3.1** Experimental and simulated PXRD patterns of SrTaO$_2$N nanowire (ICSD 95373) thin films and the simulated PXRD pattern of Ta (ICSD 96594).

Metal oxide precursors can be converted to (oxy)nitrides at elevated temperatures and ammonia flow (e.g., SrTaO$_2$N derived from Sr$_2$Ta$_2$O$_7$). Figure 3.3.1 displays
The experimental and simulated PXRD patterns of SrTaO$_2$N nanowire grown on tantalum substrate. The nanowire film was mechanically scratched from the substrate to avoid reflection peaks from binary tantalum nitride. The PXRD patterns reveal the SrTaO$_2$N nanowires crystallizes with the space group $I4/mcm$ (140).

![SEM micrograph of a SrTaO$_2$N/TiO$_x$/Ni(OH)$_x$/CoP$_i$ nanowire photoanode on a tantalum substrate.](image)

**Figure 3.3.2** SEM micrograph of a SrTaO$_2$N/TiO$_x$/Ni(OH)$_x$/CoP$_i$ nanowire photoanode on a tantalum substrate.

SEM measurements were carried out to observe the morphology of the SrTaO$_2$N photoanode after coating with three overlayers in the form of TiO$_x$, Ni(OH)$_x$, and CoP$_i$. As shown in Figure 3.3.2, one-dimensional nanowire structure was clearly observed even coating with three serial coating steps. As a result of high nitridation temperature at 1273 K, partially sintering can be found from the nanowires. The nanowire thin film is not perpendicularly oriented with several micrometers thick. As shown in Figure 3.3.3, a band gap of 2.25 eV was determined by means of UV-Vis spectroscopy, which is close to previous reports values on SrTaO$_2$N.

![Tauc plot for direct allowed transition for nanowire photoanode.](image)

**Figure 3.3.3** Tauc plot for direct allowed transition for nanowire photoanode.
A complementary TEM analysis on the nanowires was carried out due to the insufficiency of SEM to detect the overlayers. A high-angle annular dark field (HAADF) STEM micrograph of the SrTaO$_2$N nanowire is presented in Figure 3.3.5a. In Figure 3.3.5a, the regions of higher average atomic number or larger thickness appear brighter in terms of the mass-thickness contrast. Both the EELS and EDX data sets were simultaneously acquired from this exact region. The elemental abundance maps in Figure 3.3.5b were produced from the EELS data according the procedure outlined in the section of 3.2.3. In Figure 3.3.5b, the relative concentration of C, N, O, Ti, Sr, and Ta are displayed within the region defined in Figure 3.3.5a. Particularly of the Ti map, the signal is observed only in the outer edges of the nanowire in this 2D projection. The reason could be a higher concentration of Ti atoms along the edges due to the experimental geometry of the 2D projection, which would hint a core-shell structure. The core region lacks Ti signal due to the low relative concentration of Ti, which would cause the Ti-L$_2$,L$_3$ edges used for the mapping to fall below the experimental noise level due to plural scattering.

![Figure 3.3.4 EDS maps from the region investigated in Figure 3.3.5.](image)

Figure 3.3.5c presents the compositional line profile from the magenta lines in Figure 3.3.5a,b. Figure 3.3.5d shows the relative concentrations of the six presented elements along with the absolute thickness. It is evident that both the Ti and O signals in the shell region is in enrichment as their correlation. The O present in the underlying C film leads to an offset of the percent composition that increases the relative amount in the nanowire region. The stoichiometry of the nanowire was estimated to be close to the expected ratio of Sr/Ta/O/N 1:1:2:1 by subtracting the offset.

As presented in Figure 3.3.5d, the morphology and thickness of the nanowire are nicely visualized in the form of a relief map. Multiple smaller particles or grains that agglomerating within the nanowire could be observed in combination with the HAADF micrograph. It can be seen from the EELS maps that the O concentration appears to follow this particle morphology, as does the surface morphology. While this may suggest that the TiO$_x$ shell encompasses all of these individual particles, future work would be needed to draw this conclusion. It should be noted that this visualization is not a true 3D representation of the nanowire but is merely intended to emphasize the morphology.
Figure 3.3.5 (a) HAADF micrograph of a SrTaO$_2$N/TiO$_x$/Ni(OH)$_x$/CoP$_i$ nanowire. (b) EELS maps of C, N, O, Ti, Sr, and Ta from the same region as in (a). (c) Line profiles for each of the elements as well as the absolute thickness extracted from the magenta lines in (a) and (b). (d) Thickness of this region after conversion to nanometers, visualized as a relief map. (e) Mean EDX spectra from two different spatial regions of the nanowire. The light-gray spectrum comes from the shell, and the dark-red spectrum comes from the core. The exact regions used to extract these spectra are denoted in the EDX signal mask (inset). The gray labels correspond to impurities in the TEM that are unrelated to the nanowire. It should be noted that the presence of Co and Ni is below the detection limit for spatial mapping in EELS but is visible in the corresponding EDX spectra.

In order to prove the nanowire particles were encapsulated by a shell of the Ti visible at the edges of this 2D projection, the EDX data were acquired simultaneously, as presented in Figure 3.3.5e. Here, Ti map of EELS analysis was used to create two spatial masks (inset) which are used to average out the EDX spectra in the shell and core regions, respectively. Figure 3.3.5e shows the resulting averaged spectra of Ti, indicating the presence of Ti signal in both regions. In the shell region, the ratio of Ti/N is approximately 0.20, and falls to 0.02 in the core region. In combination with EELS maps, it can be concluded that the shell of the
nanowire must be Ti-rich and that this encapsulates the entire wire. These are strong evidence in favor of the presence of the hypothesized core-shell structure. The thickness of the TiO\textsubscript{x} encapsulating layer was estimated between 1 and 3 nm according to these data. The presence of Co and Ni is not visible in EESL due to the low detection limit for spatial mapping. But they are visible in the corresponding EDX analysis as shown in Figure 3.3.5e.

**Figure 3.3.6** XP spectra of Ta 4p, N 1s (a), Ti 2p (b), O 1s (c), and Co 2p (d) for SrTaO\textsubscript{2}N/TiO\textsubscript{x}/Ni(OH)\textsubscript{x}/CoP\textsubscript{i} nanowire photoanode.

The XPS was employed to investigate the surface composition of the SrTaO\textsubscript{2}N nanowire photoanode with overlayers. The corresponding high-resolution spectra for the selected regions are presented in Figure 3.3.6. The Figure 3.3.6a shows the core levels of Ta 4p and N 1s which were detected in the range of binding energies (E\textsubscript{b}) between 394 and 412 eV; the N 1s shows characteristic of metal (oxy)nitrides at such low E\textsubscript{b} which is agreement with previous reports.\textsuperscript{97} The Ti 2p\textsubscript{1/2} was overlapped with Ta 4p\textsubscript{1/2} at E\textsubscript{b} = 465.3 eV, as displayed in Figure 3.3.6b. As such, the peak is a superposition of Ta 4p\textsubscript{1/2} and Ti 2p\textsubscript{1/2} photoemission. The lower E\textsubscript{b} of 459.3 eV for Ti 2p\textsubscript{3/2} is the characteristic of TiO\textsubscript{2} although it is shifted toward higher binding energy.\textsuperscript{106,107} As shown in Figure 3.3.6c, the O 1s spectrum splits into two peaks at 530.7 and 532.4 eV. The main peak at 530.7 eV indicates lattice O\textsuperscript{2−}, whereas
the minor peak at 532.4 eV corresponds to hydroxyl\textsuperscript{108} and oxynitride\textsuperscript{109} species. Due to the tiny surface concentration of nickel, it is practically invisible. The spectrum of Co 2p is shown in Figure 3.3.6d. The peak at 781.3 eV can be attributed to Co 2p\textsubscript{3/2}, and its high $E_b$ value suggests Co-P instead of Co-O bonding.

### 3.3.2 Photoelectrochemical Water Oxidation

![Figure 3.3.7](image1.png)  
**Figure 3.3.7** Mott-Schottky plot of the TiO\textsubscript{x}/FTO electrode in pH 13 0.1 M NaOH aqueous solution at an AC amplitude of 10 mV frequency of 1000 Hz.

![Figure 3.3.8](image2.png)  
**Figure 3.3.8** LSV of Ta/SrTaO\textsubscript{2}N nanowire photoanode with TiO\textsubscript{x} overlayer in pH 13 0.1 M NaOH electrolyte at a scan rate of 10 mV s\textsuperscript{-1} under chopped light AM 1.5G illumination.

Amorphous TiO\textsubscript{x} was chosen as the initial protective overlayer for the oxynitride from photocorrosion. The deposition of TiO\textsubscript{x} overlayer can stabilize the (oxy)nitride Ta\textsubscript{3}N\textsubscript{5}.
electrodes similarly to the function of ferrihydrite layer on SrTaO$_2$N. An FTO/TiO$_x$ electrode was prepared and its Mott-Schottky plot was measured to investigate the properties of TiO$_x$ (see Figure 3.3.7). The Mott-Schottky plot displays nonlinear behavior, indicating multiple electronic states in the band gap, which is characteristic of a blocking layer$^{24}$, in accordance with the XPS results.

The particular coating effects on the SrTaO$_2$N performance were first studied by means of LSV experiments, separately. As shown in Figure 3.3.8, the curvature of the Ta/SrTaO$_2$N nanowire photoanode LSV curve did not display noticeable change after coating with TiO$_x$ layer. The photocurrent developed a strong increase upon illumination and stabilized at a certain value after an exponential decrease. Noticeable dark current also shows up in the SrTaO$_2$N nanowire photoanode on tantalum substrate, which is common in oxynitride photoanodes prepared on a tantalum substrate and is proposed to be the processes at the semiconductor surface.$^{97,110}$

![Figure 3.3.9 LSV of Ta/SrTaO$_2$N nanowire photoanode with Ni(OH)$_x$ overlayer in pH 13 0.1 M NaOH electrolyte at a scan rate of 10 mV s$^{-1}$ under chopped light AM 1.5G illumination.](image)

It is known that a electrodeposited Ni(OH)$_x$ layer on the surface of Ta$_3$N$_5$ can store photogenerated holes and sever as an passivation layer to prevent photocorrosion. When comparing the Ni(OH)$_x$-coated SrTaO$_2$N photoelectrode with the bare SrTaO$_2$N photoelectrode from the LSV curves shown in Figure 3.3.9, the dark current declines close to zero. Over the light off and on, the LSV curves of SrTaO$_2$N and SrTaO$_2$N/Ni(OH)$_x$ show an instantaneous spike, which originates from the recombination of photogenerated holes at the photoelectrode surface with conduction band electrons.$^{59}$ An addition electrocatalyst of CoP$_i$ was explored since the TiO$_x$ or Ni(OH)$_x$ did not improve the net photocurrent during PEC water oxidation. Photoassisted electrodeposition can deposit CoP$_i$ on the active sites of the semiconductors. In Figure 3.3.10, CoP$_i$-modified bare SrTaO$_2$N nanowire photoanode and the
bare SrTaO$_2$N were compared. The dark current deteriorated after coating with CoP$_i$, and it is still quite above zero, indicating photocorrosion.

![Graph](image1.png)

**Figure 3.3.10** LSV of Ta/SrTaO$_2$N nanowire photoanode with CoP$_i$ overlayer in pH 13 0.1 M NaOH electrolyte at a scan rate of 10 mV s$^{-1}$ under chopped light AM 1.5G illumination.

![Graph](image2.png)

**Figure 3.3.11** LSV of SrTaO$_2$N nanowire photoanodes with TiO$_x$, Ni(OH)$_x$, and CoP$_i$ overlays in pH 13 0.1 M NaOH electrolyte at a scan rate of 10 mV s$^{-1}$ under chopped light AM 1.5G illumination.

Given the different functions of the above-described overlayers, it would be worth integrating the blocking layer TiO$_x$, the passivation layer Ni(OH)$_x$, and the cocatalyst layer CoP$_i$ layer by layer to modulate the SrTaO$_2$N nanowire to build core-shell nanostructured photoanodes. Figure 3.3.11 shows the LSV curves of one same SrTaO$_2$N nanowire photoanode integrated with TiO$_x$, Ni(OH)$_x$, CoP$_i$ layers. After integrating three different functional layers, the photocurrent boosted significantly to 0.27 mA cm$^{-2}$ at 1.23 V versus RHE. The dark current
was also suppressed simultaneously to the same level as for the SrTaO$_2$N/Ni(OH)$_x$ photoanode. These means that the surface passivation and water oxidation kinetics augment can be achieved concurrently.

**Figure 3.3.12** LSV of SrTaO$_2$N nanowire photoanodes with Ni(OH)$_x$ and CoP$_i$ overlayers in pH 13 0.1 M NaOH electrolyte at a scan rate of 10 mV s$^{-1}$ under chopped light AM 1.5G illumination.

**Figure 3.3.13** CA of SrTaO$_2$N nanowire photoanodes with TiO$_x$, Ni(OH)$_x$, and CoP$_i$ overlayers in pH 13 0.1 M NaOH electrolyte at 1.23 V versus RHE under chopped light AM 1.5G illumination.

When comparing SrTaO$_2$N/Ni(OH)$_x$/CoP$_i$ photoanode with SrTaO$_2$N/TiO$_x$/Ni(OH)$_x$/CoP$_i$ as shown in Figure 3.3.12, one interesting characteristic could be observed. The SrTaO$_2$N/Ni(OH)$_x$/CoP$_i$ photoanode lacking TiO$_x$ blocking layer only developed a photocurrent around 0.1 mA cm$^{-2}$ at 1.23 V versus RHE. These results reveal that the intermediate TiO$_x$ layer between the oxynitride core and the consecutive shells is highly required to realize a synergetic effect for amended charge separation. The recombination of photogenerated
electron-hole pairs can be suppressed by the intermediate TiO$_x$ layer, producing a higher concentration of holes available for water oxidation processes.$^{24}$

Figure 3.3.13 presents the CA curves at 1.23 V versus RHE for SrTaO$_2$N nanowire photoanode with and without overlayers modification. The SrTaO$_2$N nanowire photoanode only deposited with amorphous TiO$_x$ develops high dark current, which is almost 50% to the total current of 0.075 mA cm$^{-2}$. After decorated with the electrocatalytic CoP$_i$ layer, the composite SrTaO$_2$N nanowire photoanode establishes a photocurrent of 0.25 mA cm$^{-2}$ with the dark current close to zero.

Prolonged CA also was carried out to test the stability of the composite oxynitride core-shell SrTaO$_2$N nanowire photoanode, shown in Figure 3.3.14. After running for around two hours, the photocurrent was decreased slightly with negligible dark current.

![Figure 3.3.14 Prolonged CA of SrTaO$_2$N nanowire photoanodes with TiO$_x$, Ni(OH)$_x$, and CoP$_i$ overlayers in pH 13 0.1 M NaOH electrolyte at 1.23 V versus RHE under AM 1.5G illumination interrupted four times.](image)

### 3.4 Conclusions

In this chapter, a quaternary oxynitride core-shell nanowire SrTaO$_2$N/TiO$_x$/Ni(OH)$_x$/CoP$_i$ photoanode was designed and the core-shell structure was analyzed. Three distinct functional overlayers were integrated with the SrTaO$_2$N nanowire to build an efficient structure. In the core-shell structure, TiO$_x$ can reduce surface charge-carrier recombination and protect SrTaO$_2$N from photocorrosion, Ni(OH)$_x$ can store photogenerated holes and CoP$_i$ acts as electrocatalyst for water oxidation. The synergetic hole extraction from the oxynitride core to the catalyst surface can thus be realized by the sequential coating.

The core-shell composite SrTaO$_2$N/TiO$_x$/Ni(OH)$_x$/CoP$_i$ photoanode develops a photocurrent of 0.27 mA cm$^{-2}$ at 1.23 V versus RHE for water oxidation with a zero-close dark current. The work in this chapter highlights an efficient core-shell structure based on
oxynitride to extract holes to the surface while simultaneously enabling efficient electron transport along the nanowire.
Exploring the Origins of Improved Photocurrent by Acidic Treatment for Quaternary Tantalum-Based Oxynitride Photoanodes on the Example of CaTaO$_2$N

4.1 Introduction

Nitrogen containing carbodiimides and metal (oxy)nitrides are prospective n-type semiconducting candidates for PEC water splitting because of their usually narrower band gaps.$^{111,112}$ The well-known Ta$_5$N$_5$ has a band gap of 2.1 eV and has achieved an experimental photocurrents which is very close to its theoretical limit of 12.9 mA cm$^{-2}$. However, its onset potential at 0.6 V versus RHE remains much higher than its flat band potential of −0.2 V versus RHE. The perovskite-related structure of quaternary oxynitrides AB(O,N)$_3$ (A = La, Ca, Sr, Ba; B = Ta, Nb) have alterable band gap from 1.7 to 2.4 eV along with the chemical composition.$^{21,97,113}$ An SrTaO$_2$N nanowires photoanode with functional overlayers forming a hole-extraction gradient has been designed in Chapter 3.

Generally, quaternary tantalum-based oxynitrides show better photocatalytic performance than niobium-based oxynitrides. The higher activities are proposed to originate from the higher chemical stability of Ta$^{5+}$, compared to Nb$^{5+}$, which more easily gets reduced to Nb$^{4+}$. Conversely, the reduced Ti$^{3+}$ at the surface region induces high photocatalytic activity for titanium-based oxynitride LaTiO$_2$N. Domen et al.$^{114}$ has increased the photochemical activity for LaTiO$_2$N by twofold via post-treating the material in aqua regia for a short period of time. The improvement is proposed from surface restructuration under strong acidic conditions. Under the strong acidic conditions, the inactive surface layer regions can be removed and Ti$^{4+}$ can be reduced to Ti$^{3+}$ in the rearranged surface region. The excess BaO on BaTaO$_2$N was also removed by acidic treatment.$^{110}$

The surface properties of Ta$_5$N$_5$ play an essential role on its photocatalytic activity because a 2 nm thick TaN layer forming from reduced tantalum ions exists on its surface. Severe recombination of charge carriers occurs at the surface due to the reduced TaN layer. The photocatalytic water splitting can be improved by removing this surface layer with acidic treatment. It is interesting to note that XPS results have suggested the presence of oxygen in these acid etched samples, but infrared spectroscopy is insufficient to prove the occurrence of hydroxyl species.$^{115}$

In order to prepare large scale of oxynitride photoactive materials, solid state reaction at high ammonolysis temperature is the most common used method. Adding a suitable flux such as chloride salts NaCl into the reaction system can lower the temperature for ammonolysis reaction remarkably by providing a molten medium facilitating ionic diffusion. In some cases, the flux can also affect the morphology of the product crystal by increasing the crystal growth rate.$^{116}$ Because of the smaller radius Ca$^{2+}$ cation comparing with Sr$^{2+}$ cation,
CaTaO$_2$N crystallizes in space group $Pnma$ with higher structural distortion than SrTaO$_2$N crystallized in space group $I4/mcm$. Figure 4.1.1 displays the crystal structure of SrTaO$_2$N and CaTaO$_2$N, the symmetry changes from tetragonal to orthorhombic.

Figure 4.1.1 The crystal structure of SrTaO$_2$N (a) and CaTaO$_2$N (b). Strontium, tantalum, calcium, oxygen and nitrogen atoms are drawn in red, green, purple, blue and gray, respectively.

The tailoring surface properties of oxynitrides is a critical aspect to obtain efficient hole extraction. In this chapter, the typical quaternary Ta-based oxynitrides CaTaO$_2$N was used as example to study the acidic treatment effect on its PEC behavior. The CaTaO$_2$N can be classified as a n-type semiconductor chemically lying between Ta$_3$N$_5$ and LaTiO$_2$N. The compound has a band gap of 2.4 eV with yellow color. Thus, its photocatalyst properties for either water splitting$^{118-120}$ or CO$_2$ reduction,$^{121}$ have been investigated, as well as a nontoxic yellow pigment.$^{122}$ The CaTaO$_2$N was assembled into photoelectrode for PEC water oxidation. The enhanced performance by acidic treatment was explored by using complementary physical characterization techniques, such as XPS, EIS and $^1$H and $^{14}$N solid-state NMR.

4.2 Experiments

4.2.1 Synthesis of CaTaO$_2$N

The conventional solid-state reaction method was used to synthesize $\text{Ca}_2\text{Ta}_2\text{O}_7$ precursor. The ground $\text{CaCO}_3$ (99 wt %, Grüssing GmbH) and $\text{Ta}_2\text{O}_5$ (99.85 wt %, abcr GmbH) were burned at a ramping rate of 10 K min$^{-1}$ to 1343 K for 24 h under air atmosphere. After cooling to room temperature at a rate of 10 K min$^{-1}$, the white color $\text{Ca}_2\text{Ta}_2\text{O}_7$ was obtained.

In order to convert $\text{Ca}_2\text{Ta}_2\text{O}_7$ oxide precursor to corresponding oxynitride, 700 mg as-prepared white $\text{Ca}_2\text{Ta}_2\text{O}_7$ powder was milled together with a flux of 300 mg NaCl (99.5 wt %, Grüssing GmbH) and 300 mg KCl (99.5 wt %, Grüssing GmbH). The mixed powder was
nitridated in a tube furnace under a constant flow of NH$_3$ (15 mL min$^{-1}$) and H$_2$ (5 mL min$^{-1}$) at 1273 K for 15 h at a ramping rate of 10 K min$^{-1}$. The residual flux agents were removed by washing thoroughly with water. The final yellow product was dried in an oven at 333 K for 8 h.

4.2.2 Etching of CaTaO$_2$N Powders

Fresh aqua regia was prepared by mixing HCl (~37%, Fisher Chemical) and HNO$_3$ (65%, Fisher Chemical) in ratio of 3:1. In order to etch CaTaO$_2$N, 200 mg powder was immersed into 4 mL aqua regia under stirring for 20 s. Then, the suspension was diluted immediately with 1 L of distilled water, rinsed thoroughly during subsequent filtration and dried at 333 K for 8 h. The treated sample was labeled as CaTaO$_2$N-A.

4.2.3 Fabrication of CaTaO$_2$N Photoanodes

The prepared powder samples were assembled into photoelectrode via electrophoretic deposition (EPD) process. Briefly, homogeneous suspension was obtained by sonicating the mixture of 24 mg CaTaO$_2$N powder, 6 mg of iodine and 30 mL of acetone. Precleaned FTO slides or titanium foil were used as substrate to deposit the oxynitride particle-based photoanodes. The two substrates were inserted into the suspension with 1 cm distance, and direct voltage of 25 V was applied for 4 min. The prepared oxynitride photoanode was dried naturally, followed by dropping 10 μL of 10 mM TaCl$_5$ (99 wt%, abcr GmbH) methanol solution. After dried, the procedure was repeated four times. The photoelectrode was annealed at 723 K for 1 h under a constant flow of NH$_3$ (15 mL min$^{-1}$) and H$_2$ (5 mL min$^{-1}$). The procedure is so called necking treatment.

4.2.4 Electrodeposition of the NiB$_3$ Overlayer

A nickel borate (NiB$_3$) cocatalyst was deposited onto the photoelectrode surface by a modified procedure in literature.$^{123}$ The electrodeposition was carried out at a constant potential of 1.21 V versus 1 M Ag/AgCl for 15 s from a electrolyte pH at 9.2 of 1 mM Ni(NO$_3$)$_2$ and 0.1 M potassium borate (KB$_3$) buffer. After deposition, the electrode was washed with deionized water.

4.2.5 Transmission Electron Microscopy

To investigate the chemical homogeneity and morphology, a transmission electron microscopy (TEM) sample was prepared by mechanically removing a part of the CaTaO$_2$N particles from the photoanode. The sample was investigated with a Themis Z TEM (Thermo Fisher) equipped with a SuperX EDX detector operated at 300 kV in the scanning TEM mode.
4.2.6 Solid State NMR

The $^1$H and $^{14}$N magic angle spinning (MAS) NMR experiments were performed at the magnetic field $B_0 = 14.1$ T (Larmor frequencies of 600.12 and 43.36 MHz for $^1$H and $^{14}$N, respectively) and MAS rate $v_r = 60.00$ kHz on a Bruker Avance-III spectrometer equipped with 1.3 mm MAS probe head. The $^1$H acquisitions involved rotor synchronized, double-adiabatic spin-echo sequence with 90° 1.25 $\mu$s excitation pulse followed by two 50.0 $\mu$s tanh/tan high-power adiabatic pulses with 5 MHz frequency sweep. All pulses operated at the nutation frequency $v_{\text{nut}} = 200$ kHz. 1024 signal transients with 5 s relaxation delay were accumulated for each spectrum. The relaxation delay of 5 s together with the total pulse sequence duration of 133 $\mu$s were used and verified to provide quantitative spectra. Shifts were referenced with respect to neat tetramethylsilane. The $^{14}$N NMR spectra was recorded with a single-pulse (“Bloch-decay”) protocol using a 3.0 $\mu$s excitation pulse with a nutation frequency of 78 kHz. 65536 scans with 1 s relaxation delay were collected for each spectrum. $^{14}$N shifts were referenced with respect to solid NH$_4$Cl.

4.3 Results and Discussion

4.3.1 Structural Characterization

![Figure 4.3.1 Experimental and simulated PXRD patterns of Ca$_2$Ta$_2$O$_7$ (ICSD 93847).](image)

The Ca$_2$Ta$_2$O$_7$ was successfully synthesized by conventional solid-state method, PXRD confirmed the single phase as shown in Figure 4.3.1. The oxide precursor was converted to oxynitride via high temperature annealing under ammonia atmosphere. Figure 4.3.2 shows the PXRD patterns of CaTaO$_2$N before and after etching. The PXRD pattern identifies phase pure product of CaTaO$_2$N. After etched in aqua regia, the PXRD pattern does not display any distinct differences in the diffraction angles and peak intensities, indicating the structural
stability under aqua regia treatment for a short period of up to few minutes similarly to LaTiO$_2$N.$^{114}$ The optical properties were investigated by means of UV-Vis absorption, as shown in Figure 4.3.3. After post treatment in aqua regia, the UV-Vis absorption edge remains almost unchanged and lies around 500 nm which is agree with pervious report values.$^{120}$

![Experimental and simulated PXRD patterns of CaTaO$_2$N and CaTaO$_2$N-A (ICSD 411139).](image1)

**Figure 4.3.2** Experimental and simulated PXRD patterns of CaTaO$_2$N and CaTaO$_2$N-A (ICSD 411139).

![Tauc plot for indirect allowed transition for CaTaO$_2$N and CaTaO$_2$N-A.](image2)

**Figure 4.3.3** Tauc plot for indirect allowed transition for CaTaO$_2$N and CaTaO$_2$N-A.

The CaTaO$_2$N particle morphology was observed by means of SEM after assembled into photoelectrode. As show in Figure 4.3.4, cubic particles in size of nano-to micrometer range covered the photoelectrode. Some pores can be observed on the cubes, which have been reported on other oxynitride during transforming from oxides at high temperature.
Pervious works have reported that the photocatalytic performance of LaTiO$_2$N$^{114}$ and Ta$_3$N$_5$$^{115}$ can be improved by removing the inactive surface layers with aqua regia etching. However, no evidence of the presence of surface hydroxyl groups after etching was provided by the using analytic methods such as XPS and Fourier-transform infrared spectroscopy (FT-IR) in neither of cases. Due to the low sensitivity of the surface composition changes by etching effect, quantitative description is lacking to prove the etching effect for these two materials. The etching of TaN or amorphous TaO surface layer is believed to be the reasons of photochemical activity enhancement for binary nitride. The sophisticated solid-state NMR technique was employed here to understand the etching effect related to PEC performance based on quaternary oxynitride.

![Figure 4.3.4 SEM micrograph of a CaTaO$_2$N photoanode on the Ti substrate.](image)

**Figure 4.3.4** SEM micrograph of a CaTaO$_2$N photoanode on the Ti substrate.

Figure 4.3.5 Solid-state NMR spectra at 60 kHz MAS of $^1$H for CaTaO$_2$N powder samples before and after etching.

![Figure 4.3.5 Solid-state NMR spectra at 60 kHz MAS of $^1$H for CaTaO$_2$N powder samples before and after etching.](image)
In Figure 4.3.5, the pristine and etched CaTaO$_2$N perovskite oxynitrides were characterized by means of the quantitative $^1$H MAS NMR spectra. The measurements were carried out on powder samples, that is before assembled into a thin film electrode. Two $^1$H signals can be clearly seen from the patterns, i.e. proton species in terminating hydroxyl moieties in inorganic surfaces at the chemical shift around 1 ppm, as well as the one from different adsorbed water layers at 4-7 ppm. Attractively, remarkable signal intensity in the spectral resonance 1 ppm was observed on the aqua regia treated CaTaO$_2$N sample, revealing higher concentration of terminating OH groups. On the other side, the signal intensities in the spectral region of 4-7 ppm related also increased after etching. These results establish the meaningful surface modulation over aqua regia etching, and therefore approve the conclusion that these perfunctory alterations are major factors to the enhanced PEC activity. Particularly, the $^1$H MAS NMR spectra reveals that no hydrogen was incorporated into the CaTaO$_2$N structure even NH$_3$ and H$_2$ gases were used as a reactive source during nitridation.

Figure 4.3.6 shows the $^{14}$N MAS NMR spectra for CaTaO$_2$N powder samples before and after etching. For both samples, only one single resonance at 270 ppm was observed, in accordance with previous reports.$^{127,128}$ This signal sticks proximity impeccably to a single Lorentzian function with full width at half maximum (fwhm) of 210 Hz, suggesting an absence of any significant structural/occupational disorder.

The $^{14}$N spectrum seems to be not affected by aqua regia etching, excepting a tiny expansion in the baseline width of the peak. $^{14}$N is an integer-spin ($I = 1$) nucleus which usually presents substantial resonance broadening in consequence of the interaction between the nuclear quadrupolar moment and the electric-field gradient from the nearby electron density. However, the absence of spinning sidebands at 60 kHz MAS implies a very weak interaction.

![Figure 4.3.6 Solid-state NMR spectra at 60 kHz MAS of $^{14}$N for CaTaO$_2$N powder samples before and after etching.](image)
This is verified by acquiring the $^{14}$N NMR spectra on static samples, which display quite narrow resonances with fwhm of $\sim 1450$ Hz. These suggest a quadrupolar interaction that is basically zero owing to the high symmetry of the nitrogen position in CaTaO$_2$N, which is consistent with earlier research.$^{127,128}$ Contrastingly, the $^{14}$N MAS spectra could not detect the existence of binary TaN phase which contains partially reduced tantalum ions, comparing with earlier works on the Ta$_3$N$_5$ photocatalyst. The results suggest that the origin of the performance improvement after acidic treatment (see below) is different for quaternary tantalum-based oxynitrides. Theoretically, the $^1$H and $^{14}$N NMR spectra can detect the presence of any paramagnetic Ta$^{4+}$ ions formed from Ta$^{5+}$ reduction during aqua regia etching, this can be observed through the peaks shifting from the main resonances by a paramagnetic shift. In case of etched CaTaO$_2$N, any such additional resonances were observed, indicating that there is no evidence for Ta$^{5+}$ reduction.

**Figure 4.3.7** XP spectra of Ta 4f for the assembled Ti/CaTaO$_2$N-A/NiB$_i$ photoanode (including necking treatment).

**Table 4.3.1** Binding energies of Ta 4f$_{5/2}$ and Ta 4f$_{7/2}$ peaks for the identified Ta$_3$N$_5$, TaON, and Ta$_2$O$_5$ species.

<table>
<thead>
<tr>
<th>composition</th>
<th>Ta 4f$_{5/2}$ (eV)</th>
<th>Ta 4f$_{7/2}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta$_3$N$_5$</td>
<td>27.0</td>
<td>24.8</td>
</tr>
<tr>
<td>TaON</td>
<td>27.7</td>
<td>25.7</td>
</tr>
<tr>
<td>Ta$_2$O$_5$</td>
<td>29.1</td>
<td>27.0</td>
</tr>
</tbody>
</table>

XPS was employed to analyze the surface composition of CaTaO$_2$N-A/NiB$_i$ photoanode. The Ta 4f spectrum is shown in Figure 4.3.7. The spectrum was deconvoluted.
into three doublets, which are summarized in Table 4.3.1. The analysis reveals a multiphase composition, such as Ta$_3$N$_5$, Ta$_2$O$_5$, and TaON. Nitride and oxide anions surround the Ta$^{5+}$ presence, which is in accordance to the coordination of tantalum ions in CaTaO$_2$N. The XPS also did not show any peaks of reduced forms from Ta$^{5+}$ cations.

The Ca 2p XPS is depicted in Figure 4.3.8, the Ca 2p$_{3/2}$ and Ca 2p$_{1/2}$ peaks centered at 346.5 and 349.8 eV. The peaks indicate that calcium atoms are rather atoms in oxygen-hydroxide systems than in salts (e.g., nitrate, chloride, carbonate or sulphate) because $E_b$ values of the Ca 2p$_{3/2}$ peak in salts usually locates in the range 347.1-348.6 eV.

![Ca 2p XPS spectrum](image1)

**Figure 4.3.8** XP spectra of Ca 2p for the assembled Ti/CaTaO$_2$N-A/NiB$_i$ photoanode (including necking treatment).

![Ta 4p and N 1s XPS spectrum](image2)

**Figure 4.3.9** XP spectra of Ta 4p and N 1s for the assembled Ti/CaTaO$_2$N-A/NiB$_i$ photoanode (including necking treatment).
Restating the features of XPS focusing surface analysis, these evidences reveal the concentration of terminating OH groups of CaTaO$_2$N was increased, even after necking procedure. The result is in agreement with the above $^1$H and $^{14}$N MAS NMR results. Figure 4.3.9 presents the XPS Ta 4p peak accompanied by the N 1s signal. The N 1s peak locates at ca. 395.4 eV with low intensity due to the low ammonolysis temperature for the necking step. It should be noted that the XPS could not detect the nickel overlayer from the electrodeposition because of low surface concentration.

![Figure 4.3.10 HAADF micrograph of the Ti/CaTaO$_2$N-A/NiB$_i$ photoanode.](image)

**Figure 4.3.10** HAADF micrograph of the Ti/CaTaO$_2$N-A/NiB$_i$ photoanode.

![Figure 4.3.11 EDX spectra from the same area of Figure 4.3.10. Peaks of interest are labelled in black while peaks representing measurement artifacts (Cu from the TEM grid, Fe and Al from the stainless steel) are colored in gray.](image)

**Figure 4.3.11** EDX spectra from the same area of Figure 4.3.10. Peaks of interest are labelled in black while peaks representing measurement artifacts (Cu from the TEM grid, Fe and Al from the stainless steel) are colored in gray.

The HAADF related to TEM was used to further analyze the assembled CaTaO$_2$N-A/NiB$_i$ photoanode as shown in Figure 4.3.10. The CaTaO$_2$N-A/NiB$_i$ was mechanically scratched from
the electrode surface for the characterization, the HAADF overview reveals a large agglomerate. Energy dispersive X-ray spectroscopy was recorded at each probe site by scanning the region. The presences of Ca, Ta, O, and N in CaTaO$_2$N have been proved by the EDX spectra, and the distribution of the elements are chemically homogenous over the agglomerate. Figure 4.3.11 shows the integration over all region of the EDX spectra. The signal belonging to nickel can be clearly seen from the spectra, suggesting successfully NiB$_x$ cocatalyst deposition.

### 4.3.2 Photoelectrochemical Water Oxidation

![Graph showing LSV of Ti/CaTaO$_2$N photoanode](image1)

**Figure 4.3.12** LSV of Ti/CaTaO$_2$N photoanode without necking treatment in pH 13 0.1 M NaOH electrolyte at a scan rate of 10 mV s$^{-1}$ under chopped light AM 1.5G illumination.

![Graph showing LSV of FTO/CaTaO$_2$N photoanode](image2)

**Figure 4.3.13** LSV of FTO/CaTaO$_2$N photoanode with necking treatment in pH 13 0.1 M NaOH electrolyte at a scan rate of 10 mV s$^{-1}$ under chopped light AM 1.5G illumination.
Two individual types of photoelectrodes were fabricated by assembling with CaTaO$_2$N before and after acidic treatment. Post-necking procedure was added for both cases by TaCl$_5$ impregnation and ammonolysis at low temperature in order to enhance the interparticle electric conductivity.\textsuperscript{130}

![Figure 4.3.14 LSV of CaTaO$_2$N, CaTaO$_2$N-A with necking treatment, and composite photoanodes, containing a NiB$_i$ catalyst, CaTaO$_2$N/NiB$_i$ and CaTaO$_2$N-A/NiB$_i$ in pH 13 0.1 M NaOH electrolyte at a scan rate of 10 mV s$^{-1}$ under chopped light AM 1.5G illumination.]

The small CaTaO$_2$N cubic particles were built into a thin film photoelectrode on titanium substrate via EPD process. Without post-necking treatment, only very low photocurrents were exhibited on this metallic substrate as shown in Figure 4.3.12. Comparing the different substrate FTO and titanium for CaTaO$_2$N deposition (Figure 4.3.13 and Figure 4.3.14), the metallic Ti substrate with CaTaO$_2$N particle-base thin film after necking developed higher photocurrent. This is the consequence of more favorable interfacial transfer for photoelectrodes prepared on metallic titanium substrate.\textsuperscript{131} The NiB$_i$ OER cocatalyst overlayer was electrochemically deposited onto the CaTaO$_2$N particle-base thin film photoelectrode. As shown in Figure 4.3.14, all the fabricated photoelectrodes develop an anodic photocurrent over LSV measurements under illumination. The CaTaO$_2$N photoelectrodes show initial photocurrent at around 0.2 V versus RHE similarly to many other quaternary oxynitrides due to the negative flat band potential, such as SrNbO$_2$N.\textsuperscript{132} A cathodic current was observed at the initial low potentials, similarly to porous TaON on Ti substrates\textsuperscript{133} described as the capacitive current.\textsuperscript{134} The photoelectrodes developed enhancement in photocurrent after necking treatment which increased the interparticular electric conductivity (see above). The photocurrent of CaTaO$_2$N photoelectrode was strongly improved after the acidic etching, both visible for the electrode with and without NiB$_i$ OER cocatalyst. An OER cocatalyst can increase the reaction kinetics by effectively using of
holes,\textsuperscript{135} thus an improved photocurrent at ca. 40 μA cm\(^{-2}\) at 1.23 V versus RHE was achieved on the etched CaTaO\(_2\)N electrode with NiB\(_i\) as cocatalyst. The etching and cocatalyst effects were also reflected in the CA curves measured at 1.23 V versus RHE as shown in Figure 4.3.15. A higher percentual augment of photocurrent was reached by cocatalyst deposition on the acid etched oxynitride comparing to the pristine CaTaO\(_2\)N. These results suggest that hole transfers faster from the light absorbing layer to the cocatalyst due to the acidic modification of the oxynitride surface.

![Figure 4.3.15 CA of CaTaO\(_2\)N, CaTaO\(_2\)N-A with necking treatment, and composite photoanodes, containing a NiB\(_i\) catalyst, CaTaO\(_2\)N/NiB\(_i\) and CaTaO\(_2\)N-A/NiB\(_i\) in pH 13 0.1 M NaOH electrolyte at 1.23 V versus RHE under chopped light AM 1.5G illumination.](image)

![Figure 4.3.16 Nyquist plots fitting for CaTaO\(_2\)N before and after etching measured at 1.0 V versus RHE under AM 1.5G illumination.](image)
The EIS and Mott-Schottky measurements were also performed to study the water oxidation process further. The typical EIS Nyquist plots, which measured at 1.0 V versus RHE under illumination, are depicted in Figure 4.3.16. The Nyquist plot arc radius can be used to estimate the interface layer resistance arising at the surface of the electrode, a higher charge transfer efficiency usually is accompanied with a smaller arc radius. As can be seen from Figure 4.3.16, the CaTaO$_2$N photoanode after aqua regia etching shows a diminished arc radius, indicating reduced charge transfer resistance and accelerated electron transfer. Thus, a higher photocurrent was achieved after etched (Figure 4.3.15). In both the pristine and etched CaTaO$_2$N photoanode cases, the arc radiuses were declined after deposition of NiBi cocatalyst overlayer.

In both the pristine and etched CaTaO$_2$N photoanode cases, the Mott-Schottky plots show positive slopes, indicating the n-type semiconducting behavior of CaTaO$_2$N (Figure 4.3.17). The etched CaTaO$_2$N photoanode has an obvious shift of the flat band potential value comparing with the pristine one. The CaTaO$_2$N before and after etching develop a flat band potential of −0.59 V versus RHE and −0.62 V versus RHE, respectively. Previous work also reported a change of surface band bending after aqua regia treatment on the model of p-type GaN. This behavior could also be accounted for the acid-etched CaTaO$_2$N particles.

![Figure 4.3.17 Mott-Schottky plot of CaTaO$_2$N before and after etching measured at 10 Hz in the dark.](image)

### 4.4 Conclusions

In this chapter, CaTaO$_2$N has been used as example to study the origin of enhanced PEC performance after acid etching for Ta-based quaternary oxynitrides. The prepared and etched CaTaO$_2$N has been constructed into photoanodes and solid-state NMR, XPS, PEC and EIS have been used to investigate the origin of advanced photocurrent. The $^{14}$N NMR spectra reveals a high symmetry of the nitrogen signal for the prepared and etched CaTaO$_2$N, no other form of (oxy)nitride phases was detected. Instead, $^1$H NMR spectra indicates a more
heterogeneous surface with a significantly higher concentration of terminating OH groups after acid etching, which induces improvement in photocurrent. The simple surface modulation ameliorates the charge transfer at the semiconductor-catalyst interface for the CaTaO$_2$N-A/NiB photoanode and as a consequence boosts the photocurrent. The reasons of performance enhancement are different from pervious report on LaTiO$_2$N. The work in this chapter highlights the applications of solid-state NMR spectroscopy for the understanding of the bulk and surface chemistry in order to design efficient heterojunction photoanodes.
5 Mössbauerite as Iron-Only Layered Oxyhydroxide Catalyst for \( \text{WO}_3 \) Photoanodes

5.1 Introduction

The PEC efficiency is severely hindered by the OER due to the sluggish kinetics of the four proton/electron-coupled transfer process on photoanode for water oxidation.\(^{137}\) Thus, it is called for developing superior OER electrocatalysts to modify photoanode to overcome the bottleneck reaction. Given the cost-effective factors, no rare element such as iridium should be used as cocatalysts, or the loading amount has to be minimized. In the searching of OER electrocatalysts for PEC water oxidation, the abundance of iron element is only slightly lower than Si, Al, and O in the earth crust,\(^{138}\) but the iron-based electrocatalysts have not been explored as broadly as other transition metals such as Ni and Co.

Several thin iron-based overlayers, such as FeOOH,\(^{139}\) FeNiO\(_x\),\(^{140}\) and ferrihydrite,\(^{141}\) have been explored and demonstrated as efficient catalytic overlayers to advance the PEC performance for photoanodes. The oxyhydroxide ferrihydrite in nano-size can enhance the photocurrent for different semiconducting oxide and nitride photoanodes.\(^{142}\) In case of an SrTaO\(_2\)N nanowire thin-film photoanode, the ferrihydrite overlayer has been proven to act simultaneously as a protective coating and hole storage layer.\(^{97}\) Layered double hydroxides (LDH) are facile to synthesize, versatility in chemical composition, and structural morphologies are easy to adjust, making them a promising class of materials for electrocatalysis, and photocatalysis, or as precursor for oxidic catalysts.\(^{143}\)

Recently, an iron-only layered oxyhydroxide i.e. mössbauerite has been investigated as electrocatalyst for water oxidation, a current density of 10 mA cm\(^{-2}\) at 1.63 V versus RHE.\(^{144}\) The layers in mössbauerite are of CdI\(_2\)-type (Fe\(^{11+}\)\(_6\)O\(_4\)(OH)\(_8\)[CO\(_3\)]\(_3\)H\(_2\)O) which carry a positive charge and are spaced by carbonate for charge balance. Only iron metal element containing material mössbauerite can be synthesized using H\(_2\)O\(_2\) to green rust in a fast chemical oxidation process. The green color product is an iron-only LDH with a Fe\(^{2+}/\text{Fe}^{3+} = 2:1\) mixed-valence.\(^{145}\) During the formation of mössbauerite in the oxidation process, partial deprotonation to an oxyhydroxide takes place in the meantime.

As an intrinsic semiconductor, mössbauerite has a narrow enough band gap to absorb visible light. Mössbauerite could be used to construct heterojunctions owing to its strong light absorption, purely semiconducting behavior, and the layered oxyhydroxide structure. In this chapter, the as-synthesized mössbauerite was investigated as potential cocatalyst for PEC water oxidation on semiconductor \( \text{WO}_3 \) thin film photoanode.
5.2 Experiments

5.2.1 Synthesis of Mössbauerite

All chemicals were provided by Sigma-Aldrich. A previously reported method was used to prepare mössbauerite.\textsuperscript{146} Shortly, argon-saturated deionized water was used to dissolve ferrous (2.65 g, 99.9%) and ferric chloride hydrate (1.75 g, 99.9%) yielding a total iron concentration of 0.4 M. Another argon-saturated water dissolved Na\textsubscript{2}CO\textsubscript{3} solution of 1 M was prepared. Subsequently, the Na\textsubscript{2}CO\textsubscript{3} solution was added to iron solution under continuous argon flow at 323 K, the final suspension was green and stirred for 30 mins at 323 K. Afterwards, 2 mL of a 30 wt\% H\textsubscript{2}O\textsubscript{2} solution was poured in one shot and the color of the suspension changed to brownish-red. Finally, the obtained mössbauerite suspension was washed with distilled water and freeze-dried. The product can be stored in air atmosphere.

5.2.2 Synthesis of WO\textsubscript{3} Photoanodes

An FTO (2.2 mm thick, Sigma-Aldrich) glass substrate was used to grow WO\textsubscript{3} thin film photoanode according to a previous procedure with a slight modification.\textsuperscript{147} Firstly, 10 mL of 0.1 M H\textsubscript{2}C\textsubscript{2}O\textsubscript{4} (99%) solution and 5 mL of 0.1 M Na\textsubscript{2}WO\textsubscript{4}·2H\textsubscript{2}O (99.995%) were prepared. The Na\textsubscript{2}WO\textsubscript{4} was added dropwise into H\textsubscript{2}C\textsubscript{2}O\textsubscript{4}, followed by adding 10 mL of 1 M HCl into the mixture under ultrasonication. Then, 6 ml of the above solution was taken off and transferred into a 20 mL Teflon-lined autoclave. A precleaned FTO glass slide was inserted into the autoclave with the conductive side downward. After the autoclave was sealed and put in an oven, the temperature was heated up to 453 K and kept at this temperature for 2 h. The FTO slide was removed from the autoclave after cooling down to the room temperature and washed with deionized water. After the FTO slide was dried, the slide with deposited thin film was annealed at 823 K for 2 h under ambient atmosphere in order to increase the crystallinity of the tungsten trioxide.

5.2.3 Modification of WO\textsubscript{3} Photoanode with Mössbauerite

Ethanol was used to re-disperse the as-synthesized mössbauerite powder to obtain a concentration of 35.0 μg mL\textsuperscript{-1} by ultrasonication. The as-prepared WO\textsubscript{3} thin film photoelectrode was put on a hot plate at 323 K and the mössbauerite dispersion was deposited by conventional drop-casting onto the surface of WO\textsubscript{3}. The electrode was dried for 24 h.

5.2.4 Deposition of Mössbauerite on FTO

A homogeneous suspension of mössbauerite was used to deposit via EPD process onto FTO to get a particle-based thin film electrode. The homogeneous suspension was prepared by sonicating the mixture of 5 mg of iodine, 20 mg of mössbauerite powder and 30 mL of
acetone for 30 min. Two FTO glass slides were vertically inserted into the suspension at a
distance of 5 mm, and a 20 V of bias was applied between them for 5 min. After the EPD
process, the FTO slides were removed and dried naturally.

5.2.5 Transmission Electron Microscopy

The TEM image of Figure 5.3.3 was acquired by using a Zeiss/LEO EM922 Omega
transmission electron microscope. While the results presented in Figure 5.3.12 were obtained
on an aberration-corrected Themis Z instrument from FEI company operated at 300 kV. The
STEM mode with a convergence angle of 19.5 mrad and a collection angle of 17 mrad was
operated to acquire the HAADF and EELS results. The selected-area electron diffraction
pattern (SAEDP) was collected with a parallel illumination and a selected area entrance
aperture centered over an agglomerate. Both core-loss and low-loss EELS was simultaneously
acquired. The spectrum in Figure 5.3.13 was stripped of the pre-edge background and
deconvolved to represent a single scattering distribution.

5.3 Results and Discussion

5.3.1 Structural Characterization

![Experimental and simulated PXRD patterns of WO₃ (ICSD 16080). The inset shows the crystal structure of WO₃.](image)

**Figure 5.3.1** Experimental and simulated PXRD patterns of WO₃ (ICSD 16080). The inset shows the crystal structure of WO₃.

PXRD was first carried out to determine the as-prepared thin film photoelectrode. To
this end, the thin films were manually scratched from the substrate to avoid the interference
from tin oxide reflection peaks. As shown in Figure 5.3.1, the patterns indicate a single pure
phase i.e. tungsten trioxide, belonging to space group P 1 2/n 1 (see the inset).
Synchrotron high-energy X-ray diffraction of the highly disordered carbonate interlayered müssbauerite was reported in previous literature. The results pointed out a turbostratic disordered layered material with a d-spacing of 7.0 Å. As reported as electrocatalyst, the lack of an integral 001-series might be related to an interstratification of varying d-spacings. The valence band and conduction band are mainly contributed from O 2p and Fe 3d orbitals, respectively. The TEM results revealed that the as-prepared müssbauerite has 2D structure with intergrown hexagonal nanoplatelets. The nanoplatelets have the length around 50-200 nm and thickness around 10-20 nm, respectively. SEM was used to observe the WO₃/müssbauerite composite photoanode. The tungsten trioxide shows plates morphology, and the morphology remains unaltered after
decoration with small amount of mössbauerite. The plates are several micrometers in size and have a thickness of ca. 200 nm. Furthermore, all the plates have visible nanopores.

The UV-Vis diffuse reflectance spectroscopy was used to determine the band gap of WO\textsubscript{3} and mössbauerite. The Tauc plot of WO\textsubscript{3} is shown in Figure 5.3.2, indicating an optical bandgap of ca. 2.7 eV. In case of mössbauerite, the optical band gap was determined to be 1.85 eV for indirect allowed transition, as displayed in Figure 5.3.3. The bandgap values could be slightly affected by an Urbach tail due to the less crystalline domains or defect states, which are frequently encountered in semiconducting materials.\textsuperscript{150}

### 5.3.2 Photoelectrochemical Water oxidation

![Figure 5.3 4 Mott-Schottky plots of mössbauerite measured at different frequencies.](image)

![Figure 5.3.5 Schematic diagram of the band alignment in the tungsten trioxide and mössbauerite type-II heterojunction photoanode for water splitting.](image)
The Mott-Schottky measurements were performed at 10, 100, and 1000 Hz to evaluate the flat band potential of mössbauerite, as presented in Figure 5.3.4. The Mott-Schottky plots show positive slopes, indicating an n-type semiconducting behavior for mössbauerite. The intercepts of the plots are close to each other, and the flat band potential could be estimated to be at ca. 0.34 V versus RHE. The value is comparable with other iron-based oxide and hydroxide species. Taking hematite, for example, the flat band potential values vary from 0.71 to 0.47 V versus RHE depending on the sample preparation and morphology. The flat band potential would shift negatively along with the hydroxide content increasing. As an iron oxyhydroxide, mössbauerite is closer to ferrihydrite, which has a flat band potential around 0.3 V versus RHE.

Figure 5.3.5 depicts the energy band diagram of WO₃ and mössbauerite according to the resulting valence band edge and conduction band edge. The VB and CB difference in the composite would build a type-II heterojunction upon contact of both n-type semiconductors, as shown in Figure 5.3.5. The charge carrier separation could be enhanced owing to the formation of the interfaces between two semiconductors with different band edge positions. The open-circuit potential of WO₃ before and after mössbauerite functionalization were measured and compared in Figure 5.3.6. The heterojunction developed larger photoinduced potential drop than that of pure WO₃. The difference of the photoinduced potential drop is highly likely the more negative CB position of the mössbauerite comparing to WO₃.

![Figure 5.3.6 Open-circuit photovoltage of WO₃ and WO₃/Mössbauerite photoanodes upon light on and light off.](image)

The mössbauerite particle-based thin film on FTO was measured the PEC characters in 0.1 M Na₂SO₄ (pH 7) at a scan rate of 10 mV s⁻¹ under chopped light AM 1.5G illumination, as depicted in Figure 5.3.7. The film only developed a small anodic current density around 15 μA cm⁻² at 1.23 V versus RHE and almost no response upon illumination. No photo response may
be due to low electronic conductivity, and (or) fast surface recombination of charge carriers at interconnected mössbauerite nanplatelets.

**Figure 5.3.7** LSV of bare mössbauerite on FTO in pH 7 0.1 M Na₂SO₄ electrolyte at a scan rate of 10 mV s⁻¹ under chopped light AM 1.5G illumination.

A WO₃ thin film photoanode with very good PEC water oxidation performance was prepared by using a modified synthesis of Diao,¹⁴⁷ a photocurrent of 1.44 mA cm⁻² at 1.23 V versus RHE was achieved as shown in Figure 5.3.8. The onset potential is ca. 0.65 V versus RHE whereas the photocurrent appears for PEC water oxidation. It is hard to determine directly the number of photogenerated holes reaching the electrode-electrolyte interface due to a kinetically demanding process of water oxidation. While the oxidation of sulfite anions

**Figure 5.3.8** LSV of comparison of bare WO₃ and WO₃/mössbauerite in the presence of sulfite anions (50 mM) as hole scavenger; (b) comparison of bare WO₃ and WO₃/mössbauerite. The black curves and red curve correspond to PEC water oxidation without sulfite addition.
to sulfate anions is a very fast process which is contrary to water oxidation. Thus, the number of surface-reaching holes available for oxidative processes can be determined by using sulfite as hole scavenger. A photocurrent of 1.64 mA cm\(^{-2}\) at 1.23 V versus RHE is generated over the neat WO\(_3\) photoanode when oxidizing sulfite instead of water, as depicted in Figure 5.3.8a. The heterojunction photoanode with the functionalization of mössbauerite develops a small but significant increase in photocurrent density during sulfite oxidation at a potential below 1.15 V versus RHE. These results indicate the charge carrier separation at the WO\(_3\)/mössbauerite heterojunction is improved.

![Figure 5.3.9 LSV of WO\(_3\) photoanode with stepwise addition of mössbauerite in pH 7 0.1 M Na\(_2\)SO\(_4\) electrolyte at a scan rate of 10 mV s\(^{-1}\) under chopped light AM 1.5G illumination.](image)

The WO\(_3\)/mössbauerite heterojunction photoanode also develops a similar tendency of an improved photocurrent density during PEC OER in the absence of sulfite, as shown in Figure 5.3.8b. After coating with mössbauerite, an enhancement in photocurrent of the WO\(_3\) photoanode was recorded. As displayed in Figure 5.3.9, the photocurrent decreased after the coating amount exceeding 4 μg of mössbauerite.

The decrease of photocurrent after the catalyst reaching the optimized amount is a frequent observation for composite electrodes. The exceeded addition of catalyst leads to a decrease of the exposing to the electrolyte of the semiconductor-catalyst interfaces. Though mössbauerite can lead an enhancement in photocurrent for WO\(_3\) photoanode, the catalytic improvement of the current density remains lower than the value obtained for the sulfite oxidation (see Figure 5.3.8). The bare WO\(_3\) photoanode develops a higher current for sulfite oxidation comparing to the heterojunction electrode at more positive potential exceeding the thermodynamic potential for water oxidation (1.23 V versus RHE). This phenomenon often happens for the tungsten trioxide-based composite photoelectrodes.\(^{44}\)
Figure 5.3.10 CA of WO₃ and WO₃/mössbauerite photoanodes in pH 7 0.1 M Na₂SO₄ electrolyte at 1.23 V versus RHE under chopped light AM 1.5G illumination.

Figure 5.3.10 shows the CA curves of WO₃ and WO₃/mössbauerite photoanodes at 1.23 V versus RHE under interrupted illumination. After modified with mössbauerite, the WO₃ photoanode developed an advanced photocurrent by 10% from 1.11 to 1.22 mA cm⁻². Both the WO₃ and WO₃/mössbauerite photoanodes exhibited a slightly decay in photocurrent, which could be mainly attributed to WO₃ because of the similar shape of curvature for the two photoanodes.

Figure 5.3.11 CA of mössbauerite in pH 7 0.1 M Na₂SO₄ electrolyte at 1.23 V versus RHE under chopped light AM 1.5G illumination.

The iron oxyhydroxide ferrihydrite is known as a very efficient hole storage layer. When comparing the curvature of the CA, the difference between mössbauerite and the iron oxyhydroxide ferrihydrite is clear. The current of WO₃/mössbauerite photoanode falls to zero
without the occurrence of a cathodic overshoot (i.e., a current drop below zero accompanied by a subsequent rapid rise to zero) upon illumination interruption. The mentioned cathodic overshoot is the characteristic behavior of a hole storage layer such as provided by ferricydrite. As depicted in Figure 5.3.11, the separate bare mössbauerite electrode did not develop any noticeable photocurrent at 1.23 V versus RHE.

The mössbauerite catalytic interface after PEC water oxidation was analyzed further. Here, a separate pure mössbauerite particle-base electrode was measured for water oxidation at 1.23 V versus RHE for 60 min. Then, the sample was scratched from the substrate and dispersed in hexane in order to deposit on TEM grid. Figure 5.3.12 presents the corresponding HAADF micrograph and SAEDP. The inset in yellow is the rotational average of this diffraction pattern, and the overlaid in black is the simulated powder diffraction pattern. The high background, which is contributed from the amorphous carbon rings due to the deposition of mössbauerite plates on the thin amorphous carbon TEM grid, obscures some of the weaker reflections. Nevertheless, some of reflections corresponding to strongly diffracting atomic planes are visible, and these are annotated with dashed rings over part of the figure. These rings are accompanied with miller indices. The outer three rings have two indices each. Thus, multiple strong reflections are presented in the angular range and cannot be individually distinguished in this data set.

![Figure 5.3.12](image)

**Figure 5.3.12** (a) HAADF micrograph of a mössbauerite nanoplates after PEC measurement at 1.23 V versus RHE. (b) SAEDP from the mössbauerite nanoplates. A rotational average of this SAEDP is in the inset and selected reflections are indexed.

The EELS of agglomerated mössbauerite nanoplates after PEC OER is presented in Figure 5.3.13. The primarily +3 oxidation state is strongly suggested by the energy-loss near-edge fine structure (ELNES) features for the oxygen K and iron L$_{2,3}$ edges which are both visible and bear a striking resemblance to Fe$_2$O$_3$. 

67
The EIS spectrum for WO$_3$ and WO$_3$/Mössbauerite photoanode was measured under illumination, the results are presented in Figure 5.3.14. The heterojunction photoanode displays a smaller arc radius than that of pure WO$_3$, indicating faster charge transfer upon mössbauerite functionalization. Thus, the enhanced performance of mössbauerite-functionalized WO$_3$ photoanode could be ascribed to (i) faster charge carrier separation as
the result of the type-II heterojunction formation and (ii) an augmented hole collection efficiency owing to mössbauerite acting as a water oxidation electrocatalyst.

5.4 Conclusions

In conclusion, the mössbauerite was investigated as a cocatalyst for PEC water oxidation on tungsten trioxide thin film photoanode. A photocurrent of 1.22 mA cm\(^{-2}\) at 1.23 V versus RHE for PEC OER was achieved after functionalization with mössbauerite on WO\(_3\). The mössbauerite has n-type semiconducting behavior according to the Mott-Schottky analysis. The flat band potential was determined to be + 0.34 V versus RHE with a band gap of 1.8 eV from UV-Vis spectroscopy.

The mössbauerite-decorated WO\(_3\) photoanodes show enhancement in charge separation according to the PEC oxidation of sulfite as hole scavenger, indicating the formation of type-II heterojunction benefits charge separation. The work in this chapter proves the semiconducting nature of mössbauerite. Furthermore, constructing band alignment could improve the photocurrent due to better charge carrier separation at the interface. These results highlight the potential of mössbauerite in the building of heterojunctions for enhancing the performance of photoanodes.
6 Elucidation of the Active Sites for Monodisperse FePt and Pt Nanocystal Catalysts for p-WSe$_2$ Photocathodes

6.1 Introduction

In order to construct tandem PEC device with two semiconductor electrodes, the electronic band gaps of p-type photocathode and n-type photoanode have to be matched with each other.\textsuperscript{152} Although many perspective n-type semiconducting materials, such as n-Si,\textsuperscript{153} BiVO$_4$,\textsuperscript{44} and quaternary oxynitrides AM(O,N)$_3$ (A = Sr, Ba; M = Ta, Nb)\textsuperscript{154} have been employed as photoanodes for PEC water oxidation, only limited series of p-type semiconductor photocathodes have been studied for PEC water reduction.\textsuperscript{155} InP,\textsuperscript{156} Si,\textsuperscript{157} Cu$_2$O\textsuperscript{158} and ternary metal oxides\textsuperscript{159} are some typical promising photocathode materials. Out of them, the transition metal dichalcogenides (TMDCs) with the general formula MX$_2$ (M = transition metal; X = chalcogen)\textsuperscript{160} have been explored for PEC water splitting due to their earth-abundance, suitable band gaps for solar energy harvesting and large absorption coefficients.\textsuperscript{161} The typical TMDCs tungsten diselenide WSe$_2$ has been investigated for solar energy conversion such as in solar cells\textsuperscript{162} and PEC water splitting.\textsuperscript{161} WSe$_2$ can be used as either photoanode or photocathode by tuning into n-type or p-type with different dopants.\textsuperscript{161} A stable photoanode in aqueous iodide solution has been established with a n-type WSe$_2$ single crystal.\textsuperscript{163} Complementarily, WSe$_2$ photocathode for PEC HER can be designed by few-layer WSe$_2$ thin film and electrically-wired single crystal WSe$_2$.\textsuperscript{39,164} It is worth mentioning that a microwave-assisted plasma method is available to prepare high purity and few-layer thin TMDCs from the elements within several minutes.\textsuperscript{149} One operative method, which could make this type of materials potentially cost-effective for the PEC HER, is exfoliating TMDCs into 2D mono- or few-layered flakes. However, the exfoliated TMDCs suffer severe photogenerated charge carrier recombination due to the high concentration of defects.\textsuperscript{160} The charge carrier recombination was proposed as a result of dangling bonds on the edges of exfoliated flakes and the non-stoichiometry in the flakes.\textsuperscript{160} Differently, the crystal step edges have been elucidated to be the active catalytic sites for the structurally related MoS$_2$.\textsuperscript{165}

A metallic tungsten substrate has been used to directly grow micron-sized single-crystal platelets of p-WSe$_2$, and served as photocathodes for the HER in acidic environments.\textsuperscript{166} The bulk crystal WSe$_2$ is still limited by its low PEC performance though it can efficiently absorb solar light as an indirect bandgap semiconductor with a bandgap of 1.2 eV.\textsuperscript{167} It is generally needed to alter the charge transfer kinetic between the semiconductor-electrolyte interface by deposition of a catalyst on the surface of semiconductor. Till now, the most common catalyst with best performance catalyst for HER is still platinum.\textsuperscript{168} This noble metal could lower the overpotential of HER owing to its mild binding and adsorption energies for protons and hydrogen, respectively. Additionally, platinum, which is superior to the
nonnoble metal HER catalyst MoS$_2$ in the stability, also has been proven highly stable in acidic electrolytes. There are serval routes to advance the catalytic properties of noble metals such as customizing the size and shape of its nanocrystals (NCs), i.e. by exposing particular crystallographic facets. The biggest drawback of Pt as electrocatalyst is the high cost and scarcity, which may hinder its broad application for PEC devices. An optional way to overcome these limitations is reducing the loading of Pt such as alloying Pt with other transition metals. FePt and NiPt alloy NCs have been demonstrated to be superior in catalytic properties compared with Pt NCs endowing with mean particle size. The overpotential for PEC HER has been lowered upon WSe$_2$ photocathodes in pervious report. The authors employed an electrochemical method to co-deposit Pt and Ru which offered a preferential deposition of the metal along the step edges of WSe$_2$.

Considering the catalytic properties of monodisperse Pt and FePt NCs are the structure-sensitivity, it is worth to investigate such nanostructures in combination with WSe$_2$ as hybrid materials. In this chapter, monodisperse FePt alloy NCs and Pt NCs with comparable size were integrated with p-WSe$_2$ single-crystal photocathodes, respectively. The different catalytic activities were compared and analyzed by chemical bonding and water adsorption on the NCs at the density functional theory (DFT) level.

6.2 Experiments

6.2.1 Growth of p-WSe$_2$ Single Crystals

The corresponding elements were first used to synthesize niobium-doped polycrystalline WSe$_2$ powder. In short, selenium (99.999 %, Sigma), tungsten (99.9 %, MaTeck) and niobium (99.9%, Chempur) were ground together, followed by sealed in a quartz ampoule under vacuum. Then, the sealed ampoule was heated at 1173 K for 72 h. The chemical vapor transport (CVT) method was used to grow single crystals, where SeCl$_4$ (99.5 % Alfa Aesar) severed as a transport agent and around 3 mg of Nb severed as dopant. A prepared polycrystalline powder was put together with SeCl$_4$ (1 mg/ml) in a quartz ampoule (15 cm length and 1.2 cm of inner diameter). Ethanol/dry ice was used for cooling the system to prevent the sublimation of SeCl$_4$ when the ampoule was evacuating and closed. The ampoule was put in a two-zone furnace with the temperatures setting to 1273 K and 1223 K. These conditions remained 7 days to obtain single crystal p-WSe$_2$ via CVT.

6.2.2 Synthesis of 2 nm FePt NCs

A modified route according to previous literature was used to synthesize FePt NCs. Briefly, oleylamine (70%, Sigma) was purified by distillation under vacuum before use. Argon gas atmosphere was used through all the sample handing. 197 mg of platinum (II) acetylacetonate (98%, abcr Chemicals) and 390 mg of hexadecanionic acid (90%, Lancaster
Synthesis) and 177 mg iron (III) acetylacetonate (>99.9% Aldrich) were put into a three-neck flask. The flask was evacuated and subsequently flushed with argon for three times. Next, 30 ml dioctyl ether were introduced and the system was flushed with argon for 40 minutes before heating up to 373 K for 20 minutes. After injecting the 0.16 ml oleylamine and 0.16 ml oleic acid, the reaction system was heated up to 568 K and hold for 30 minutes. After the solution cooling down to room temperature, 80 mL of degassed ethanol were injected into the reaction flask to precipitate the black product. The precipitate was removed by centrifugation at 8000 rpm for 10 minutes. Then, the clear yellow supernatant was discharged, and the black precipitate was re-dispersed in a solution of oleic acid, oleylamine and hexane.

6.2.3 Synthesis of 4 nm FePt NCs

A modified protocol according to previous literature was used to synthesize 4 nm FePt NCs. Standard airless conditions i.e. inert gas atmosphere was used to carried out the reaction. The three-neck flask armed with 197 mg of platinum (II) acetylacetonate and 390 mg 1,2-hexadecandiol was evacuated three times and degassed with argon again, followed by adding 20 ml dioctyl ether with an additional degassing step for 30 minutes. Prior to injecting 0.16 ml oleic acid, 0.17 ml oleylamine, and 0.13 ml of Fe(CO)₅ into the reaction system, the above solution was heated up to 373 K. The reaction system was heated up to 568 K, the solution got a black color during heating and kept under reflux for 30 minutes. After cooling down to room temperature, 60 ml of degassed ethanol was injected in the reaction flask to precipitate the black product. The dispersion was loaded in glass centrifuge tubes, which were centrifuged at 8000 rpm for 10 min. The clear yellow supernatant was discharged, and the black precipitate was re-dispersed in hexane.

6.2.4 Synthesis of 1.8 nm Pt NCs

The Pt NCs was synthesized according to synthetic route by Kunz. 25 mL ethylene glycol (99.8 %, Sigma) was used to dissolve 0.25 g of H₂PtCl₆·H₂O (40 wt % metal, ChemPur). A second solution of 25 mL ethylene glycol dissolving 0.50 g NaOH (98%, abcr Chemicals) was added into the above platinum solution under vigorous stirring. The mixed solution was heated up to 423 K under reflux for 90 minutes. After the dark colloidal solution cooling down to room temperature, eight aliquots of 1 M HCl (Sigma) was added to precipitate the product. Then, the solution was centrifuged at 12 000 rpm for 10 min and the supernatant was removed. Afterwards the NCs were dispersed in 1 M HCl. After second round centrifugation, the supernatant was removed and the NCs were re-dispersed in hexane.
6.2.5 Fabrication of p-WSe$_2$/Pt and p-WSe$_2$/FePt Photocathodes

The p-WSe$_2$ single crystals were cut into around 0.3 cm$^2$ in size. A copper wire was used to connect the crystal with Ag paint and insulated with two-part epoxy. The inset of Figure 6.3.1 shows the prepared p-WSe$_2$ photocathode. The conventional drop casting method was used to deposit cocatalysts Pt or FePt.

6.2.6 First-Principles Computations

Density-functional theory (DFT) computations were performed to investigate and compare the catalytic properties of Pt and FePt NCs. The “D3” dispersion correction$^{183}$ with Becke-Johnson damping$^{184}$ was employed on top of the PBE functional$^{185}$ to deal with water-surface interactions in surfaces and clusters. The projector augmented wave (PAW)$^{186}$ method as implemented in VASP$^{187-189}$, a 500 eV cutoff for the plane-wave expansion, and an electronic convergence criterion of $10^{-7}$ eV were used for the computations. Structural optimization was continued until residual forces fell below $5 \times 10^{-3}$ eV Å$^{-1}$. LOBSTER$^{190-193}$ was used to chemical-bonding of plane-wave data. Reciprocal space was sampled on Γ-centered grids with densities between 0.02 and 0.04 Å$^{-1}$. Structural images were built via VESTA.$^{194}$

6.3 Results and Discussion

6.3.1 Structural Characterization

Figure 6.3.1 SEM micrograph of as-prepared p-WSe$_2$. The inset depicts the p-WSe$_2$ photocathode after ohmic connection with Cu wire.

Well-shaped and nice developed WSe$_2$ single crystals were produced via CVT method using SeCl$_4$ as transport agent. Figure 6.3.1 shows SEM micrograph of the as-synthesized p-
WSe$_2$ single crystal surface, revealing a flat and very clean surface. Besides that, no obvious roughness or cavities can be observed except a very few spots (defects). A single crystal was ground into powder to collect the PXRD pattern in order to confirm the phase of the crystal. Figure 6.3.2 depicts the recorded PXRD patterns, indicating a single phase of WSe$_2$. The WSe$_2$ crystallizes in 2H structure, with the space group of the $P6_3/mmc$ in accordance with literature, as shown in the inset of Figure 6.3.2.

![Figure 6.3.2](image)

**Figure 6.3.2** Experimental and simulated PXRD patterns of p-WSe$_2$ (ICSD 40752). The inset depicts the crystal structure of WSe$_2$.

A Zeiss Libra 200 FE TEM was used to analyze the prepared NCs. As shown in Figure 6.3.3, it can be clearly seen that these Pt and FePt NCs are monodisperse with narrow size distribution. The size distributions have been analyzed and the corresponding histograms are shown in Figure 6.3.4. The Pt NCs have a mean particle size of around 1.8 nm. The two synthetic routes produced two kinds of FePt NCs with mean particle size to be around 2.3 nm and 3.7 nm, respectively. Figure 6.3.5 shows the PXRD patterns of 2 nm FePt and Pt NCs, revealing the face centered-cubic-type structure.

![Figure 6.3.3](image)

**Figure 6.3.3** TEM of 1.8 nm Pt NCs (left), 2nm FePt NCs (middle) and 4 nm FePt NCs (right).
Figure 6.3.4 Histogram of diameters of the 1.8 nm Pt NCs (left), 2 nm FePt NCs (middle) and 4 nm FePt NCs (right) obtained from TEM images.

Figure 6.3.5 Experimental and simulated PXRD patterns of synthesized Pt and FePt NCs.

6.3.2 Photoelectrochemical Water Reduction

The 2 nm FePt NCs were first used to modify the p-WSe₂ photocathode, the Figure 6.3.6 shows the LSV of FePt/p-WSe₂ photocathodes with different amount of 2 nm FePt nanocrystals (mass related to Pt). The PEC performance of the pristine p-WSe₂ photocathode and modified p-WSe₂ photocathode with optimized amount of FePt and Pt cocatalyst deposition have been further compared in Figure 6.3.7. All the photoelectrode showed a semiconducting p-type behavior, developing cathodic photocurrents due to reduction of H₂O to H₂. The pristine p-WSe₂ without cocatalyst only produced very low photocurrent of 0.27 mA cm⁻² at 0 V versus RHE. After deposition of the cocatalyst Pt NCs on p-WSe₂, the photocurrent was significantly increased and the onset potential distinctly exhibited a positive shift. A photocurrent of 2.0 mA cm⁻² at 0 V versus RHE, which was 7.4 times higher in comparison to the bare p-WSe₂ photocathode, was achieved with Pt NCs decoration. These improvements can be ascribed to the highly effective cocatalyst Pt NCs, which facilitates to
collect photogenerated electrons such as to advance PEC HER and lower the overpotential of H$_2$ formation.$^{158}$

![Figure 6.3.6 LSV of FePt/p-WSe$_2$ photocathodes with different amount of 2 nm FePt nanocrystals (mass related to Pt) in pH 4.2 0.1 M KP$_i$ electrolyte at a scan rate of 10 mV s$^{-1}$ under chopped light AM 1.5G illumination.](image)

Figure 6.3.6 LSV of FePt/p-WSe$_2$ photocathodes with different amount of 2 nm FePt nanocrystals (mass related to Pt) in pH 4.2 0.1 M KP$_i$ electrolyte at a scan rate of 10 mV s$^{-1}$ under chopped light AM 1.5G illumination.

Remarkably, the p-WSe$_2$ electrode decorated with 2 nm alloy FePt NCs outperformed the the achieved photocurrent of Pt/p-WSe$_2$ photocathode, a cathodic photocurrent of 4.0 mA cm$^{-2}$ at 0 V versus RHE was achieved. The decorated p-WSe$_2$ photocathode with 2 nm FePt exhibited around 2 times photocurrent than the one decorated with Pt NCs, and around 15 times than the pristine WSe$_2$. The higher catalytic performance of Pt based alloy than that of the pure Pt is consistent with other Pt based alloy-semiconductor photocatalyst
The reasons of better catalytic performance of Pt based alloy were related to the change of the Fermi level for the catalyst, which could promote the photogenerated electrons transferring from the semiconductor conduction band to NCs.\textsuperscript{175}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.3.8.png}
\caption{CA of p-WSe\textsubscript{2}, Pt/p-WSe\textsubscript{2}, and FePt/p-WSe\textsubscript{2} photocathodes in pH 4.2 0.1 M KP\textsubscript{i} electrolyte at 0 V versus RHE under chopped light AM 1.5G illumination.}
\end{figure}

The CA curves at 0 V versus RHE for p-WSe\textsubscript{2}, Pt/p-WSe\textsubscript{2}, and FePt/p-WSe\textsubscript{2} were also carried out, as shown in Figure 6.3.8. The CA curves also reflected the augmented photocurrent after cocatalyst deposition on p-WSe\textsubscript{2}. During the CA measurements, there were continuous bubbles released, indicating H\textsubscript{2} production.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.3.9.png}
\caption{LSV of FePt/p-WSe\textsubscript{2} photocathodes with different amount of 4 nm FePt nanocrystals (mass related to Pt) in pH 4.2 0.1 M KP\textsubscript{i} electrolyte at a scan rate of 10 mV s\textsuperscript{-1} under chopped light AM 1.5G illumination.}
\end{figure}

In order to investigate the NCs size effect on the catalytic performance, 4 nm FePt NCs were also used to modify p-WSe\textsubscript{2} photocathode, as shown in Figure 6.3.9. Comparing Figure
6.3.6 and Figure 6.3.9, it can be concluded that functionalization of the larger 4 nm FePt NCs with the p-WSe$_2$ photocathode developed a slightly smaller saturated current density (normalized surface area) than that of 2 nm FePt NCs. Thus, the mass currents were compared, as depicted in Figure 6.3.10. The mass current of the p-WSe$_2$ photocathode decorated with 2 nm FePt NCs exhibited a 4.5 times higher activity at 0 V versus RHE in comparison to modification with 4 nm FePt NCs. These results connote that the superior mass specific activity for the 2 nm FePt originates from the higher amount of exposed preferential catalytic sites for HER (see below).

![Figure 6.3.10 Pt-mass-related generated photocurrent on photocathode p-WSe$_2$ for different size of FePt NCs in pH 4.2 0.1 M KP$_i$ electrolyte at a scan rate of 10 mV s$^{-1}$ under chopped light AM 1.5G illumination.](image)

### 6.3.3 Theoretical Investigations

First-principles computations have been performed to reveal why FePt NCs exhibited better HER performance than that of pure Pt NCs when coupled to p-WSe$_2$. The following approximations were used to carried out the computations: i) HER basically takes place on the cocatalyst NCs surface rather than of the WSe$_2$ and ii) the water molecule is subsequently not protonated. The water adsorption energy on the different planes i.e. (111) and (100) surfaces and the edge between these surface facets of Pt and FePt were first calculated and compared. The three sites are illustrated in the top of Figure 6.3.11, the FePt has a more negative energy of ca. 30 kJ mol$^{-1}$ than pure Pt, indicating that FePt is preferential for H$_2$O adsorption resulting in improved H$_2$O dissociation. It should be noted that the edge sites of both Pt and FePt have a more negative adsorption energy than that of (111) and (100) surface. These means that the edges are the preferential sites for H$_2$ production.

Then the first-principles atomistic Crystal Orbital Hamilton Population (COHP) analysis of the adsorption energy was also carried out to understand the interaction strength particularly such as to identify the nature of the chemical bonding, as presented in the bottom
of Figure 6.3.11. In each diagram, the antibonding and bonding levels are represented by the spikes to the left and right, respectively. It can be concluded that the O-H interactions do not differ much since the integrated COHP (ICOHP) values for Pt and FePt on different surfaces are practically the same. Contrarily, the ICOHP values of the water surface interactions have significant difference on Pt and FePt. The bottom and the top of Figure 6.3.11 are in agreement with each other, that is the water adsorption is preferential on FePt in comparison to Pt. What’s more, the edges are the preferential sites for hydrogen production.

Figure 6.3.11 (Top) Geometries of water adsorption on Pt (and PtFe) (111), and (100) surfaces, as well as the edge between these surface facets; (bottom) corresponding chemical bonding analysis by the projected Crystal Orbital Hamilton Population technique (COHP). Intramolecular O-H interactions are shown in red, while water-surface interactions are shown in black.

Figure 6.3.12 (a) Starting positions of water above the Pt clusters, (b) lowest energy configuration of water adsorption on Pt55 and Pt147 clusters.
Moreover, the Pt clusters in different size were compared to reveal the NCs size effect on catalytic properties. For this purpose, two clusters Pt$_{55}$ (ca. 1.1 nm) and Pt$_{147}$ (ca. 1.6 nm), which have the similar size with the as-synthesized NCs, have been chosen for computation. The starting positions for water are depicted in Figure 6.3.12a. Figure 6.3.12b illustrates the Pt$_{55}$ and Pt$_{147}$ clusters model and the lowest energy configuration of water adsorption on them. Only 2 kJ mol$^{-1}$ difference of water adsorption energy on these two size clusters were computed, implying that the size of Pt NCs at this level does not critically affect the mechanism for the HER on the Pt NCs. The catalytic sites of high activity have been believed to generally associated with high electronic densities around the Fermi level.$^{196}$ The atom-projected density of states (PDOS) of Pt$_{55}$ cluster and H$_2$O were established to elucidate the catalytic property on Pt, as displayed in Figure 6.3.13 (left). It can be seen that the electron density near the Fermi level are mostly contributed by the Pt 5d orbital with a small proportion of Pt 6s. The corresponding COHP is shown in Figure 6.3.13 (right). In addition to bonding levels from the interaction between H$_2$O and the Pt metal in occupied conduction bands, one finds antibonding levels near the Fermi level.

![Figure 6.3.13](image.png)

**Figure 6.3.13** Atom projected density of states (PDOS) and projected COHP analysis of the Pt$_{55}$+H$_2$O cluster.

In order to further understand the NCs size effect on catalytic properties, a model of cuboctahedron with the face-centered-cubic structure was assumed in the initial step for Pt NCs. The following three size-dependent parameters, which determine the catalytic properties with respect to the geometric structure, have been elucidated based on the model:
(i) the surface atoms ratio $R_{Ns}$ of clusters; (ii) the ratio of atoms at edges to atoms at surfaces $R_{ed}$; and (iii) the average coordination number $N_{AV}$ of the clusters. NCs are generally modeled by Pt$_N$ clusters, where the number of Pt atoms $N$ is stated by the following equations\textsuperscript{197,198}:

$$N = (2n + 1) \times \frac{(5n^2 + 5n + 3)}{3}$$

6.3.1

where $n$ is as such a natural number with meaning of the corresponding shell number of the cluster. The various cluster’s diameters $d$ are evaluated by the following equation with $V_{Pt} = 15.1$ Å$^3$, the volume per bulk atom\textsuperscript{199}:

$$d = \left(\frac{6V_{Pt}N}{\pi}\right)^{1/3}$$

6.3.2

The catalytic properties of NCs usually have strong correlation with the number of the surface atoms and edge atoms of clusters. The number of surface atoms $Ns$ can be given by\textsuperscript{197}:

$$Ns = \frac{(30n^2 + 6)}{3}$$

6.3.3

and the ratio of atoms at edges to atoms at surfaces for a cuboctahedron is determined by\textsuperscript{200}:

$$R_{ed} = \frac{24n - 36}{10n^2 - 20n + 12}$$

6.3.4

Additionally, the amount of surface atoms is correlated with the average coordination number $N_{AV}$ of the clusters as reported by literature\textsuperscript{200}:

$$N_{AV} = 12 \frac{108n^2 - 108n + 36}{10n^3 - 15n^2 + 11n - 3}$$

6.3.5

These three size-dependent parameters corresponding to a Pt cluster with sizes from 1 to 4.5 nm have been surmised in Figure 6.3.14. When the cluster size increasing, both $R_{ed}$ and the ratio $R_{Ns}$ decline. Keeping the following items in mind: (i) the edges are the preferential sites for hydrogen production, as shown in Figure 6.3.11, and (ii) the active sites of metal NCs are generally lied on the surface, thus a better catalytic activity is reputed to be achieved for smaller clusters. The average coordination number $N_{AV}$ are rising gradually in keeping with the rise of the cluster size in agreement with the reduction of $R_{Ns}$, which is related to the lattice planes and the active sites. The first-row transition metals such as iron can downshift the d-band center of Pt in the alloy structure. The d-band downshift could modulate the bonding strength between Pt and the reactant inducing a higher catalytic activity.\textsuperscript{201}

It should be mentioned that due to the different catalyst preparation methods, the photocurrent of this chapter is lower than for p-WSe$_2$ electrodes, which have been decorated with photo-electrodeposited ruthenium/platinum catalysts by the Lewis group.\textsuperscript{39} The uniform morphology of the FePt and Pt NCs in this chapter enable an elucidation of the different HER activity for the FePt/WSe$_2$ and Pt/ WSe$_2$ interface at the molecular level in spite of the lower activity in comparison to ruthenium-platinum thin-film catalysts.
6.4 Conclusion

In conclusion, monodisperse FePt and Pt NCs as HER catalysts were used to modify a single-crystal p-type WSe$_2$ photocathode for PEC HER. The modified p-type WSe$_2$ photocathode with FePt and Pt NC catalysts exhibited an improved photocurrent of 15 and 7.4 times for the FePt and Pt NC catalysts, respectively. The two kind of NCs can improve the photocurrent and lower the overpotential simultaneously. DFT calculations were carried out to elucidate the origin of enhanced activity by investigating the electronic structure of the adsorbed H$_2$O molecules on the monometallic and alloy NCs. The water adsorption energy on alloy FePt NCs is more negative than that of single Pt NCs from the computed results. The O-H interactions do not have much difference since the ICOHP values are almost the same, while the ICOHP of water-surface interactions have been computed to have significant difference on Pt and FePt.

The FePt NC can enhance H$_2$O dissociation due to its preferential for H$_2$O adsorption in comparison to Pt NCs. The NC edges are supposed to be the active sites for H$_2$O reduction, because these sites have, both for Pt and FePt, more negative adsorption energy than those on (111) and (100) facets. Hence, the work in this chapter not only proposes the nature of the active sites for Pt-based alloys but also highlights the use of bimetallic NCs to increase the HER activity while simultaneously lowering the amount of noble metal.
7 Conclusion and Outlook

Throughout this thesis, several different strategies have been investigated, depending on the individual photoelectrode material, in order to better understand the origins for the improvement of PEC water splitting efficiency for several photoelectrodes. For the ternary oxide CuWO₄, the PEC water oxidation performance has been augmented by a facile post-annealing under nitrogen atmosphere which could improve the charge carrier separation and decrease the charge-transfer resistance. In the case of quaternary oxynitrides, a core-shell structure has been constructed by coating different functional overlayers on a SrTaO₂N nanowire photoanode. The core-shell structure with functional overlayers can reduce surface charge-carrier recombination, protect the oxynitride surface from photocorrosion and extract photogenerated holes to the electrode-electrolyte surface efficiently.

Acidic etching of quaternary oxynitrides, which was demonstrated on the example of CaTaO₂N, has proven that this strategy could induce high concentration of terminating OH groups on the surface. Thus, the charge transfer at the semiconductor-catalyst interface can be enhanced for the CaTaO₂N-A/NiB₃ photoanode; yielding an upsurge in photocurrent. The earth abundant trivalent iron-only layered oxyhydroxide mössbauerite has been demonstrated as a potential cocatalyst for PEC water oxidation on semiconductor photoanodes by coupling with a WO₃ photoanode. In case of the p-WSe₂ single-crystal photocathode, an alloy FePt NCs catalyst with low loading amount has exhibited superior catalytic performance than pure Pt NCs when decorating on p-WSe₂ photocathode for PEC HER. DFT computations reveal that the water adsorption and thus enhanced H₂O dissociation are preferential on FePt in comparison to Pt.

Scientists have put much effort to investigate PEC technology in order to better use the inexhaustible solar energy. However, the efficiency of PEC cell technology is today still far from commercial applications. The work in this thesis could provide some guidelines for a rational design of high-efficiency PEC devices targeting commercial applications. For the transition from an invention to an innovation, more efforts have to be invested in the development of integrated PEC devices. Further investigations will most likely focus on fundamental insights regarding the charge transfer properties of semiconducting photoelectrodes, the interface of photoelectrode/cocatalyst/electrolyte, and the band bending behavior. Alongside, narrow band gap semiconducting materials consisting of earth abundant elements have to be explored to achieve high stability and efficiency, as well as efficient cocatalysts to achieve a solar-to-hydrogen efficiency exceeding 10%. Such device should be wireless and consist of an intermediate transparent conductive substrate which connects dual transparent photoabsorbers operating as photoanode and photocathode, respectively. External energy supply would not be needed to split water into hydrogen and oxygen.
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