

**KINETICS AND MECHANISTIC STUDIES OF PHOTO-
INDUCED PROCESSES IN VANADATE-BASED BINARY
METAL OXIDE ELECTRODES**

BY

TAHIR NAVEED JAHANGIR

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This thesis, written by **TAHIR NAVEED JAHANGIR** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **DOCTOR OF PHILOSOPHY IN CHEMISTRY.**



Dr. Jameel R. Al-Thagfi
Department Chairman



Dr. Suliman Saleh Al-Homidan
Dean of Graduate Studies

Date _____



Dr. Tarek A. Kandiel
(Advisor)



Dr. Khalid R. Alhooshani
(Member)



Dr. Mohammad Ali Morsy
(Member)



Dr. Bassam El Ali
(Member)



Dr. Mohammad Fethouhi
(Member)

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**Dedicated to my Parents, Sisters,
Wife, kids, and my late Brother**

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LIST OF ABBREVIATIONS

LED	:	Light emitting diode
MOS	:	Metal oxide semiconductor
OEC	:	Oxygen evolution catalyst
OER	:	Oxygen evolution reaction
HER	:	Hydrogen evolution reaction
WOR	:	Water oxidation reaction
PEC	:	Photoelectrochemical
E_{fb}	:	Flat band potential
ΔG (kJ mol ⁻¹)	:	Gibbs free energy
ΔS (J K ⁻¹)	:	Change in entropy
λ (nm)	:	Wavelength
θ	:	The angle at which constructively interfering X-rays leave a crystal
η_{coll}	:	Electron collection efficiency
π	:	Pi (= 22/7)
f	:	Frequency
ω	:	Omega (= 2 π f)

W	:	Width
DL	:	Diffusion length
UV	:	Ultra-violet
SCLJ	:	Semiconductor/electrolyte junction
*	:	Transition state species
RHE	:	Reversible hydrogen electrode
CBM	:	Conduction band Maximum
VBM	:	Valence band Maximum
FTO	:	Fluorine doped tin oxide
PCD	:	Pulse current electrodeposition
DFT	:	Density Functional Theory
VASP	:	Vienna ab initio simulation package
FESEM	:	Field-emission scanning electron microscope
EDXS	:	Energy-dispersive X-ray spectroscopy
XRD	:	X-ray diffraction
XPS	:	X-ray photoelectron spectrometer
q	:	Charge
E_{tot} (defect:q)	:	Total energies of a supercell with a defect in a

		charge q
E_{tot} (perfect)	:	Total energies of a supercell without a defect in a charge q
ϵ_F	:	Fermi level
E_{applied}	:	Applied electrode potential
Ag/AgCl	:	Silver/ Silver chloride reference electrode
$E_{\text{Ag/AgCl}}^o$	:	Standard Silver/ Silver chloride electrode potential
$E_{\text{Hg/HgO}}^o$	:	Standard Mercury/ Mercury oxide electrode potential
EIS	:	Electrochemical impedance spectroscopy
IPCE	:	Incident photon-to-current efficiency
PEIS	:	Photoelectrochemical impedance spectroscopy
IMPS	:	Intensity-modulated photocurrent spectroscopy
C_{sc}	:	Space charge layer capacitance
C_{dl}	:	Double layer capacitance
M-S	:	Mott-Schottky
CV	:	Cyclic voltammetry
e^-	:	Electron
h^+	:	Holes

mol	:	Moles
M	:	Molarity
°C	:	Temperature (degree Celsius)
K	:	Temperature (Kelvin)
AM 1.5G	:	Air mass 1.5 global (100 mW cm ⁻²)
B.E.	:	Binding Energy
$E_{overall}^o$	:	Overall potential
$E_{cathode}^o$	:	Cathode potential
E_{anode}^o	:	Anode potential
eV	:	Electron Volt
PECs	:	Photoelectrochemical cells
At. %	:	Atomic percent
V _{RHE}	:	Voltage against reversible hydrogen electrode
Im (Z)	:	Imaginary component of the impedance
JCPDS	:	Joint Committee on Powder Diffraction Standards
ε	:	Relative dielectric constant
ε_0	:	Permittivity of vacuum
N _d	:	Donor density

k	:	Boltzmann constant
E	:	Applied potential
E_{tot}	:	Total energy
DOS	:	Density of states
E_{bulk}	:	Total energy of the bulk supercell
LSV	:	Linear sweep voltammetry
ABPE	:	Applied bias photo-to-current efficiency
j_{photo}	:	Photocurrent density
V	:	Applied bias potential against Pt electrode
P_{light}	:	Light intensity
TPC	:	Transient photocurrent
V_{photo}	:	Photovoltage
OCP	:	Open-circuit potential
OCP_{dark}	:	Dark open-circuit potential
$\text{OCP}_{\text{light}}$	:	Light open-circuit potential
k_s	:	Rate constant of charge transfer
C_{total}	:	Total capacitance of interfacial layer
LDH	:	Layer double hydroxide

I-V	:	Current- potential graph
I_m	:	Anodic photocurrent spike
I_s	:	Steady state photocurrent
I_t	:	Time-dependent current
SEI	:	Semiconductor-electrolyte interface
τ	:	Transient decay time
L_p	:	Hole diffusion length
W	:	Space charge carrier width
R_{SC}	:	Charge transfer resistance
R_{ct}	:	Charge transfer resistance
C_H	:	Helmholtz capacitance
HF	:	High frequency
LF	:	Low frequency
k_{tr}	:	Rate constant of charge transfer
k_{rec}	:	Rate constant of surface charge recombination
η_{ct}	:	Charge-transfer efficiency
DRS	:	Diffused reflectance spectroscopy
ΔE	:	Binding energy difference

V_{Pt} : Potential against Platinum electrode

VB : Valence band

CB : Conduction band

ABSTRACT

Full Name : [Tahir Naveed Jahangir]
Thesis Title : [Kinetics and Mechanistic Studies of Photo-induced Processes in Vanadate-Based Binary Metal Oxide Electrodes]
Major Field : [Physical Chemistry]
Date of Degree : [December 2023]

The utilization of solar hydrogen as a carbon-free chemical fuel has the potential to mitigate carbon footprints. It can be produced by photoelectrochemical (PEC) water splitting that consists of semiconductor photoelectrodes. It is known that the water oxidation half-reaction (WOR) is recognized as the rate-limiting step for hydrogen generation in the PEC cells. The pursuit of a photoactive photoanode is therefore a significant matter. Bismuth vanadate (BiVO_4) is a promising photoanode for PEC water splitting owing to its cost competitiveness, visible light reactivity, and remarkable stability in neutral and alkaline solutions. Nevertheless, the sluggish water oxidation on its surface causes severe charge carrier recombination and thus reduces the overall efficiency. Also, the reported synthetic routes for BiVO_4 photoanodes either are sophisticated or exhibit low activity. To overcome these imperfections, in this thesis, we focused on the development of a facile method for the fabrication of BiVO_4 photoanodes with improved PEC activity.

First, we prepared BiVO_4 by chemical bath deposition method and modified it with transition metal-based oxygen evolution electrocatalysts, namely, NiFe, CoNi, and CoFe-layered double hydroxides (LDHs) oxygen evolution catalysts (OECs). The kinetics of charge transfer and recombination in the prepared photoanodes were studied by transient photocurrent and intensity-modulated photocurrent spectroscopy (IMPS). The rate constants of charge transfer and recombination were determined and correlated with the generated photocurrent to disclose the function of each electrocatalyst. It was concluded

that the three investigated LDHs exhibit a comparable electrocatalytic activity, but CoNi–LDH has a superior passivation effect. Contrary to CoFe and NiFe–LDHs, CoNi –LDH passivates the surface states and unpins the Fermi level as proved by IMPS and photovoltage measurements. This study provides a systematic pathway to disclose the role of LDH OECs on BiVO₄ which is an essential step for rational designing efficient photoanodes.

Second, we developed a novel and facile solution processing method to fabricate BiVO₄ and Ti₃C₂T_x-modified BiVO₄ (Ti₃C₂T_x/BiVO₄) photoanodes. The charge transfer kinetics of the photoinduced processes within the fabricated electrodes were studied by transient open circuit potential (OCP), transient photocurrent (TPC), photoelectrochemical impedance spectroscopy (PEIS), and intensity-modulated photocurrent spectroscopy (IMPS). It was demonstrated that Ti₃C₂T_x forms a Schottky-like junction at the BiVO₄/Ti₃C₂T_x interface and acts as a hole transport/storage layer. This creates a built-in electric field that increases the band bending and space charge layer width, eventually enhancing the charge separation efficiency. Modification of Ti₃C₂T_x/BiVO₄ with a water oxidation catalyst such as cobalt phosphate (Co-Pi) was essential to deliver the maximum photocurrent. For instance, Co-Pi/Ti₃C₂T_x/BiVO₄ photoanode delivered 4.72 mA cm⁻² at 1.23 V_{RHE}, which is 2 and 11-fold higher than those of Ti₃C₂T_x/BiVO₄ and pristine BiVO₄ photoanodes, respectively. This study provides a practical protocol for fabricating Ti₃C₂T_x/BiVO₄ and reveals the role of MXene in photoelectrochemical water splitting.

The short hole diffusion length (HDL) in semiconductor photoanodes is one of the main drawbacks of BiVO₄ photoanodes, thus in the third part, we introduced a facile recipe to design a pinholes-free BiVO₄ photoanode with a NiV₂O₆ back contact interfacial (BCI)

layer, marking a significant advancement in hole-diffusion length and photoelectrochemical activity. The fabricated BiVO₄ photoanode with NiV₂O₆ BCI layer exhibits a twofold increase in the HDL compared to pristine BiVO₄. Despite this improvement, we found that the front surface recombination still hinders the water oxidation process, as revealed by photoelectrochemical (PEC) studies employing Na₂SO₃ electron donors and by intensity-modulated photocurrent spectroscopy measurements. To address this limitation, the surface of the NiV₂O₆/BiVO₄ photoanode was passivated with a cobalt phosphate electrocatalyst, resulting in a dramatic enhancement in the PEC performance. The optimized photoanode achieved a stable photocurrent density of 4.8 mA cm⁻² at 1.23 V_{RHE} which is 12-fold higher than that of pristine BiVO₄ photoanode. Density Functional Theory (DFT) simulations revealed an abrupt electrostatic potential transition at the NiV₂O₆/BiVO₄ interface with BiVO₄ being more negative than NiV₂O₆. A strong built-in electric field is thus generated at the interface and drifts photogenerated electrons toward the NiV₂O₆ BCI layer and photogenerated holes toward the BiVO₄ top layer. As a result, the back-surface recombination is minimized and ultimately the HDL is extended in agreement with the experimental findings.

Despite major developments, the PEC performance of BiVO₄ based-photoanode is still less than the theoretical value and its stability needs improvement. Generally, the quality of the developed BiVO₄ film (i.e. pinhole-free) and the electronic band structure of the created heterostructure are crucial factors. The formation of discontinuous BiVO₄ opens the pathway for the undesired back reaction at the FTO substrates (i.e. the back reduction of the photooxidized products). The focus of the fourth part is to address this challenge, we developed a facile method to create a CoV₂O₆/BiVO₄ heterostructure using a novel hybrid

chemical bath deposition and drop casting strategy. In our approach, a compact layer from Co(OH)_2 has been initially deposited on the conductive glass substrate followed by drop casting the BiVO_4 precursor. The existence of Co(OH)_2 induced the continuous construction of $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ a film without pinholes and cracks. As a result, the pristine $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ heterostructure displayed a remarkable photocurrent density of 2.35 mA/cm^2 at $1.23 \text{ V}_{\text{RHE}}$ which is 5-fold higher than the pristine BiVO_4 photoanode. Upon modification with cobalt phosphate ions (Co-Pi) water oxidation catalysts, a stable photocurrent density of 4.22 mA/cm^2 at $1.23 \text{ V}_{\text{RHE}}$ and 95% Faradaic efficiency were achieved.

ملخص الرسالة

الاسم الكامل: طاهر نفيذ جهانجير

عنوان الرسالة: دراسات حركية وميكانيكية للعمليات المحدثة بالصور في أقطاب أكسيد الفلز الثنائي القائمة على الفاناديت

التخصص: كيمياء

تاريخ الدرجة العلمية: ديسمبر 2023

إن استخدام الهيدروجين الشمسي كوقود كيميائي خالٍ من الكربون لديه القدرة على التخفيف من آثار الكربون. يمكن إنتاجه عن طريق تقسيم الماء الكهروضوئي (PEC) الذي يتكون من أقطاب كهربائية ضوئية من أشباه الموصلات. من المعروف أن نصف تفاعل أكسدة الماء (WOR) يتم التعرف عليه كخطوة تحدد معدل توليد الهيدروجين في خلايا PEC. ولذلك فإن السعي للحصول على رمز ضوئي ضوئي يعد أمرًا مهمًا. يعد فانادات البزموت (BiVO_4) بمثابة رمز ضوئي واعد لتقسيم مياه PEC نظرًا لقدرته التنافسية من حيث التكلفة وتفاعل الضوء المرئي واستقراره الملحوظ في المحاليل المحايدة والقلوية. ومع ذلك، فإن أكسدة الماء البطيئة على سطحه تسبب إعادة تركيب حاملة الشحنة بشدة وبالتالي تقلل من الكفاءة الإجمالية. أيضًا، فإن الطرق الاصطناعية المبلغ عنها للأنودات الضوئية BiVO_4 إما متطورة أو تظهر نشاطًا منخفضًا. للتغلب على هذه العيوب، ركزنا في هذه الأطروحة على تطوير طريقة سهلة لتصنيع الأنودات الضوئية BiVO_4 مع نشاط PEC محسن.

أولاً، قمنا بإعداد BiVO_4 بطريقة ترسيب الحمام الكيميائي وقمنا بتعديله باستخدام المحفزات الكهربائية لتطور الأكسجين القائمة على المعادن الانتقالية، وهي NiFe و CoNi و CoFe ذات الطبقات المزدوجة من هيدروكسيدات (LDHS) ومحفزات تطور الأكسجين (OECs). تمت دراسة حركية نقل الشحنة وإعادة التركيب في الأنودات الضوئية المحضرة بواسطة التحليل الطيفي للتيار الكهروضوئي العابر والتحليل الطيفي للتيار الضوئي المعدل الكثافة (IMPS). تم تحديد ثوابت معدل نقل الشحنة وإعادة التركيب وربطها بالتيار الضوئي المتولد للكشف عن وظيفة كل محفز كهربائي. تم التوصل إلى أن LDHS الثلاثة التي تم فحصها تظهر نشاطًا تحفيزيًا كهربائيًا مشابهًا، لكن CoNi -LDH له تأثير تخميل متفوق. على عكس CoFe و NiFe -LDHS، يقوم CoNi -LDH بإبطال الحالات السطحية

والغاء تثبيت مستوى فيرمي كما ثبت من خلال قياسات IMPS والجهد الضوئي. توفر هذه الدراسة طريقًا منهجيًا للكشف عن دور LDH OECs في BiVO_4 والتي تعد خطوة أساسية للتصميم العقلاني للأنودات الضوئية الفعالة. يعد طول انتشار الثقب القصير (HDL) في الأنودات الضوئية لأشباه الموصلات أحد العوائق الرئيسية للأنودات الضوئية BiVO_4 ، وبالتالي في الجزء الثالث، قدمنا وصفة سهلة لتصميم أنود ضوئي BiVO_4 خالي من الثقوب مع طبقة واجهة اتصال خلفية (BCI) NiV_2O_6 ، مما يمثل تقدمًا كبيرًا في طول انتشار الثقب والنشاط الكهروضوئي الكيميائي. يُظهر الرمز الضوئي BiVO_4 المُصنع مع طبقة BCI NiV_2O_6 زيادة مضاعفة في HDL مقارنةً بـ BiVO_4 الأصلي. على الرغم من هذا التحسن، وجدنا أن إعادة تركيب السطح الأمامي لا تزال تعيق عملية أكسدة الماء، كما كشفت الدراسات الكهروضوئية (PEC) التي تستخدم المتبرعين الإلكترونيين Na_2SO_3 وقياسات التحليل الطيفي للتيار الضوئي المعدلة بالكثافة. ولمعالجة هذا القيد، تم تخميل سطح الأنود الضوئي $\text{NiV}_2\text{O}_6/\text{BiVO}_4$ باستخدام محفز كهربائي من فوسفات الكوبالت، مما أدى إلى تحسين كبير في أداء PEC. حقق الأنود الضوئي المُحسن كثافة تيار ضوئي ثابتة تبلغ 4.8 مللي أمبير سم⁻² عند 1.23 V_{RHE} وهو أعلى بـ 12 مرة من كثافة الأنود الضوئي BiVO_4 الأصلي. كشفت عمليات محاكاة نظرية الكثافة الوظيفية (DFT) عن تحول محتمل كهروستاتيكي مفاجئ في واجهة $\text{NiV}_2\text{O}_6/\text{BiVO}_4$ حيث يكون BiVO_4 أكثر سلبية من NiV_2O_6 . وبالتالي يتم إنشاء مجال كهربائي قوي مدمج في الواجهة وينجرف الإلكترونات المولدة ضوئيًا نحو طبقة BCI NiV_2O_6 والثقوب المولدة ضوئيًا نحو الطبقة العليا BiVO_4 . ونتيجة لذلك، يتم تقليل إعادة التركيب على السطح الخلفي وفي نهاية المطاف يتم تمديد HDL بالاتفاق مع النتائج التجريبية.

على الرغم من التطورات الرئيسية، لا يزال أداء PEC للأنود الضوئي القائم على BiVO_4 أقل من القيمة النظرية واستقراره يحتاج إلى تحسين. بشكل عام، تعد جودة فيلم BiVO_4 المطور (أي خالي من الثقوب) وبنية النطاق الإلكتروني للبنية المتغايرة التي تم إنشاؤها من العوامل الحاسمة. يفتح تكوين BiVO_4 المتقطع الطريق للتفاعل الخلفي غير المرغوب فيه عند ركائز FTO (أي الاختزال الخلفي للمنتجات المؤكسدة ضوئيًا). ينصب تركيز الجزء الرابع على مواجهة هذا التحدي، حيث قمنا بتطوير طريقة سهلة لإنشاء بنية متغايرة لـ $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ باستخدام استراتيجية ترسيب الحمام الكيميائي الهجين وإستراتيجية الصب بالقطرات. في نهجنا، تم ترسيب طبقة مدمجة من Co(OH)_2 في البداية على الركيزة الزجاجية الموصلة متبوعة بإسقاط صب سلائف BiVO_4 . أدى وجود

$\text{Co}(\text{OH})_2$ إلى البناء المستمر لفيلم $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ بدون ثقب وشقوق. ونتيجة لذلك، أظهرت البنية المتغايرة $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ كثافة تيار ضوئي ملحوظة تبلغ 2.35 مللي أمبير/سم² عند V_{RHE} 1.23 وهو أعلى بخمسة أضعاف من الكود الضوئي BiVO_4 الأصلي. عند التعديل باستخدام محفزات أكسدة الماء أيونات فوسفات الكوبالت (Co-Pi)، تم تحقيق كثافة تيار ضوئي ثابتة تبلغ 4.22 مللي أمبير/سم² عند V_{RHE} 1.23 وكفاءة فاراداي بنسبة 95%.

1 CHAPTER ONE

INTRODUCTION

According to the latest assessment released by the Intergovernmental Panel on Climate Change (IPCC), it has been observed that global annual anthropogenic greenhouse gas emissions have experienced a 70% rise between 1970 and 2004 when considering their 100-year global warming potentials. Moreover, indisputable evidence demonstrates an escalation in worldwide mean air and ocean temperatures, the thawing of snow and ice, and a surge in global mean sea levels. The detected alterations present notable risks to our prospective sustainable development unless considerable remedies are enacted.[1]

However, there are various viewpoints asserting that the peak of oil production has either already been reached or will be reached soon.[2, 3] While there are differing forecast scenarios and expectations of a shift towards coal or natural gas as fossil fuel sources, there is a clear indication of global concern regarding energy security. This concern is primarily driven by the high concentration of these energy supplies in geographically limited areas and the growing importance of political and economic stability.[4] Furthermore, it is worth noting that the global demand for energy continues to exhibit a steady upward trend on an annual basis. This assertion is supported by the findings presented in the report published by the International Energy Agency 2011. The report, which adopts a cautious approach in its projections, anticipates a substantial one-third surge in energy demand between the years 2010 and 2035.[5]

Currently, renewable energy sources, including biomass, geothermal, ocean, solar, wind, and hydropower, contribute approximately 89 EJ/year, accounting for 17% of the total primary energy supply.[6, 7] However, it is worth noting that a significant portion of this contribution is derived from large hydropower plants and the utilization of traditional biomass, which may not align optimally with sustainability objectives. Nevertheless, based on various forecast scenarios examined by the IPCC, it is projected that renewable energy sources have the potential to yield CO₂ savings ranging from 218 to 561 gigatonnes when compared to the estimated cumulative emissions of 1530 gigatonnes CO₂ from fossil fuels and industrial activities between 2010 and 2050. This equates to a potential contribution of savings ranging from 14% to 37%.[8]

As previously mentioned, there is a growing imperative to manage global energy demands with a focus on reducing carbon emissions, ensuring security and availability, and promoting overall sustainability. Nowadays, scientists are paying more attention to renewable energy sources like hydroelectric, wind, geothermal, and solar power, which were utilized to a lesser extent. Among the array of contemporary renewable energy resources accessible for meeting these rigorous criteria, solar energy harnessed through sunlight utilization emerges as the most promising option as a future energy source to address the depletion of fossil fuels and meet the increasing global energy demand. However, their intermittent generation is a major challenge with many existing renewable energy forms.

To overcome the issues of stability and availability in diverse environments, researchers have explored various techniques to develop different chemical and electrochemical energy storage methods utilizing specific molecules. One widely used method of chemical energy

storage involves using hydrogen gas. Hydrogen gas is a potential alternative for a carbon-based fuel industry because H_2O is the only by-product of hydrogen combustion. Previously more than 90 % of hydrogen gas was produced by steam reforming of methane which accounts for $\sim 3\%$ of annual global CO_2 emissions. Hydrogen gas can be produced by using photocatalytic (PC), photoelectrochemical (PEC), photovoltaic–electrochemical (PV-EC), solar thermochemical (STC) water splitting, photothermal catalytic (PTC), and photobiological (PB) methods[9-11], which are shown in Figure 1.1. The process of hydrogen production by water electrolysis via water splitting is a highly encouraging avenue for the provision of sustainable hydrogen energy. Water splitting can be achieved through the photoelectrochemical (PEC) reaction, which utilizes an energy source capable of dissociating water molecules into O_2 and H_2 . PEC water splitting is considered an attractive method for directly producing solar fuel, like hydrogen, from water using photocatalysis techniques. Another advantage of PEC water splitting is that H_2 and O_2 are formed in separate compartments which avoids serious safety concerns.[12] The hydrogen produced is utilized in hydrogen-based boilers, and in fuel cell-based batteries, and its large portion is used in the synthesis of NH_3 , which is further utilized for fertilizers for plants.[13] The dependence on carbon footprint can be suppressed by using hydrogen. Thus, hydrogen gas plays a key role in different applied fields and proved to be a promising alternative to carbon. It should be noted here that hydrogen will be implemented in the coming future, and for this type of hydrogen economy, clean hydrogen generation should be low-cost, and substantial investment should be required to support the hydrogen fuel cell economy.[14]

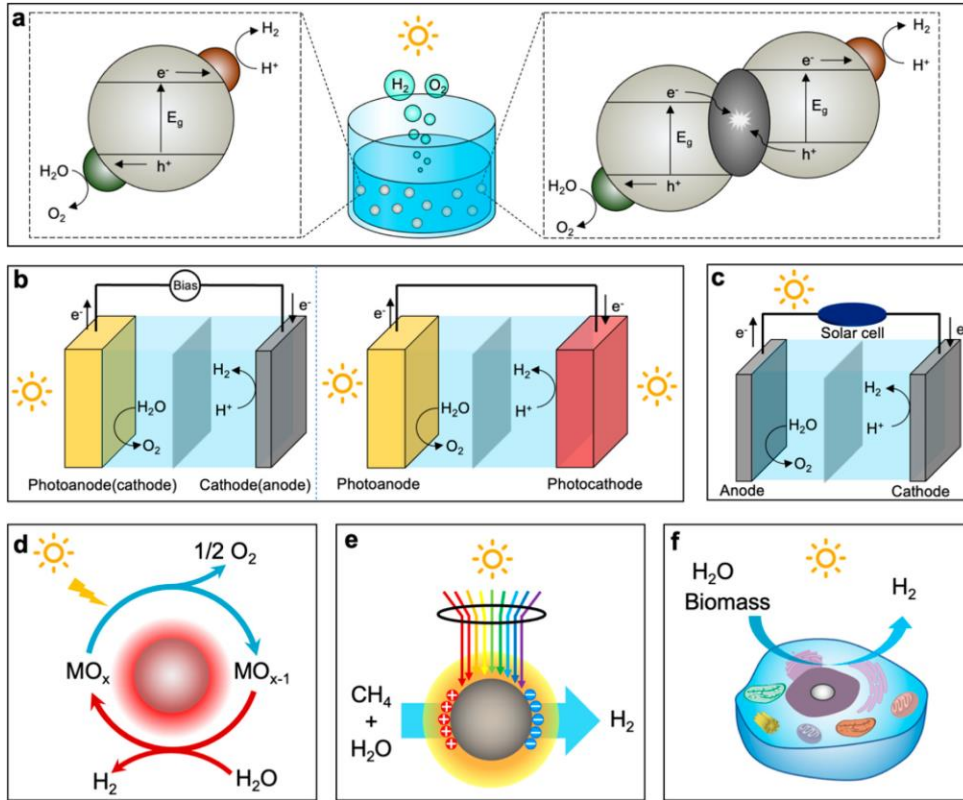


Figure 1.1. Various solar-driven H₂ production methods: (a) PC, (b) PEC, (c) PV-EC, (d) STC water splitting, (e) PTC, and (f) PB H₂ production. Adopted from ref.[15]

1.1. Basics of PEC water splitting

PEC water splitting has gained considerable interest[16], particularly due to the increasing need to produce renewable carbon energy.[17] The method involves a redox reaction in which charge carriers are produced through the absorption of solar energy at the catalyst surface, known as active sites.[18] The photoelectrodes employed in this procedure consist of semiconductors possessing a well-defined band gap, which arises from the distinct separation between the conduction band (CB) and the valence band (VB) under light illumination. The selection of a semiconductor material is heavily influenced by the positioning of its band edges. Specifically, the CB edge must possess more negative potential than the reduction potential of hydrogen, while the VB edge must have more

positive potential than the oxidation potential of oxygen to facilitate the process of water splitting. PEC water splitting involves the generation of hydrogen and oxygen gases through the dissociation of water on the surface of semiconducting materials, facilitated by the absorption of adequate solar energy and appropriate electrolysis techniques. In contrast to traditional energy generation methods reliant on fossil fuels, the utilization of photoelectrochemical (PEC) techniques for hydrogen energy production is characterized by its absence of greenhouse gas emissions.[19]

PEC water splitting involves the utilization of photoactive materials, specifically semiconductors, which are like those employed in photovoltaic cells for the purpose of generating solar electricity. The primary distinction resides in the utilization of semiconductor materials that are submerged in the process of PEC water splitting, serving as both the photoanode and photocathode. The absorption of solar light by the semiconductor results in the generation of electron-hole pairs. Subsequently, the electrons migrate towards the photocathode, where the process of hydrogen evolution takes place. This involves the combination of hydrogen ions derived from the electrolyte or those formed through the dissociation of water. The interaction between electrons and hydrogen ions produced on the surface of the semiconductor occurs via water reduction[20], whereas water is oxidized by electron acceptors known as holes. Ensuring the spatial segregation of H_2 and O_2 gas emissions is vital from a safety standpoint, and endeavors are undertaken to minimize the expenses associated with the separation of evolved gases. Figure 1.2 depicts the schematic illustration of a photoelectrochemical cell.

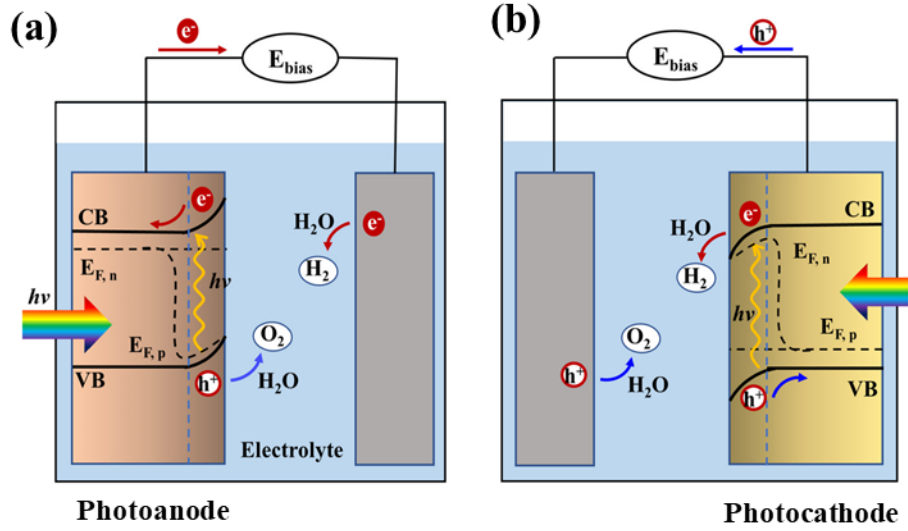


Figure 1.2. Schematic representation of a PEC cell in which the working electrodes are (a) photoanode and (b) photocathode respectively. Adopted from ref.[20]

It is anticipated that by the year 2024, there will be significant advancements in renewable PEC water-splitting technologies, resulting in efficient hydrogen generation. These advancements are projected to reduce the cost of hydrogen production to \$4.00 per gasoline gallon equivalent at the plant gate. This cost is expected to be lower than the cost of hydrogen production from petroleum oil through processes such as pyrolysis, cracking, or catalysis.[21]

Hence, PEC water-splitting presents itself as a compelling and feasible alternative for the synthesis of solar hydrogen. In order to enhance the viability of implementing PEC water splitting techniques for the industrial production of hydrogen gas, it is imperative to achieve the following criteria in the construction of an optimal PEC cell: high efficiency in terms of solar-to-hydrogen (STH) conversion, long-term and sustained stability, and minimal capital expenditure.[22]

PEC water splitting for hydrogen generation is predicated upon the utilization of solar energy and water, both of which possess the characteristic of renewability. Hydrogen possesses the potential to serve as a sustainable energy source for both stationary and transportation applications, with the advantage of a reduced carbon footprint and mitigated climate impact. Most research endeavors have been directed toward the exploration of optimal semiconductors that possess the capability to function as highly efficient photoelectrodes. Nevertheless, the objective of achieving a conversion efficiency of 10% has as far eluded attainment.

At the current level of efficiency, the generation of photocurrent at a rate of 10.0-15.0 mA cm⁻² suggests that the cost of producing hydrogen would be economically feasible and competitive with the costs associated with traditional fuels. The endurance of semiconductor materials when exposed to the electrolyte of a PEC cell is a crucial factor, with a desired level of stability set at a minimum of 2,000 operational hours. Despite multiple attempts to overcome these obstacles, practical or commercial utilization has not been attained. Therefore, it is imperative to enhance our comprehension of the underlying principles associated with PEC processes to develop highly effective photoelectrode materials that can enhance the performance of PEC water splitting. Efficiency in PEC hydrogen production is crucial to enhance sustainability. The complete utilization of solar photon energy by the semiconductor in PEC reactions is contingent upon maximizing the efficiency of PEC water splitting when exposed to visible light irradiation. This visible light irradiation corresponds to a substantial portion of 44-47% of the solar spectrum.[23] The energy derived from the absorption of light is not fully harnessed due to various electron-hole recombination processes, leading to the dissipation of energy in the form of

internal energy. Once sun photons are absorbed by photochemical materials, the resulting photoinduced electrons and holes undergo relaxation towards the band boundaries of the semiconductor. This process leads to the formation of excitons, with a portion of the energy being dissipated as heat. The recombination of charge carriers, namely photoinduced electrons and holes, is a significant process that leads to energy dissipation in the context of PEC systems. To enhance the efficiency of hydrogen production, it is imperative to create photochemical materials that optimize the absorption of solar light (photons) and reduce the recombination of charge carriers.[22, 24, 25] In this thesis, we focus on various hydrogen production pathways utilizing the PEC method, specifically focusing on the utilization of BiVO_4 semiconductors.

1.1.1. Development of BiVO_4 photoanodes

Many semiconductor photoelectrodes (e.g., Fe_2O_3 [26, 27], BiVO_4 [28, 29], TiO_2 [30], WO_3 [31], ZnO [32], CuO [33], and C_3N_4 [34]) have attracted significant attention due to their potential application in PEC hydrogen production. However, as illustrated in Figure 1.3, some of them have band positions just aligned either with water oxidation (e.g., WO_3 , Fe_2O_3 , BiVO_4) or with water reduction (e.g., Si , Bi_2S_3 , GaAs , GaP , CuO). Consequently, the central challenge persists as the development of suitable materials remains pivotal for enhancing PEC performance.

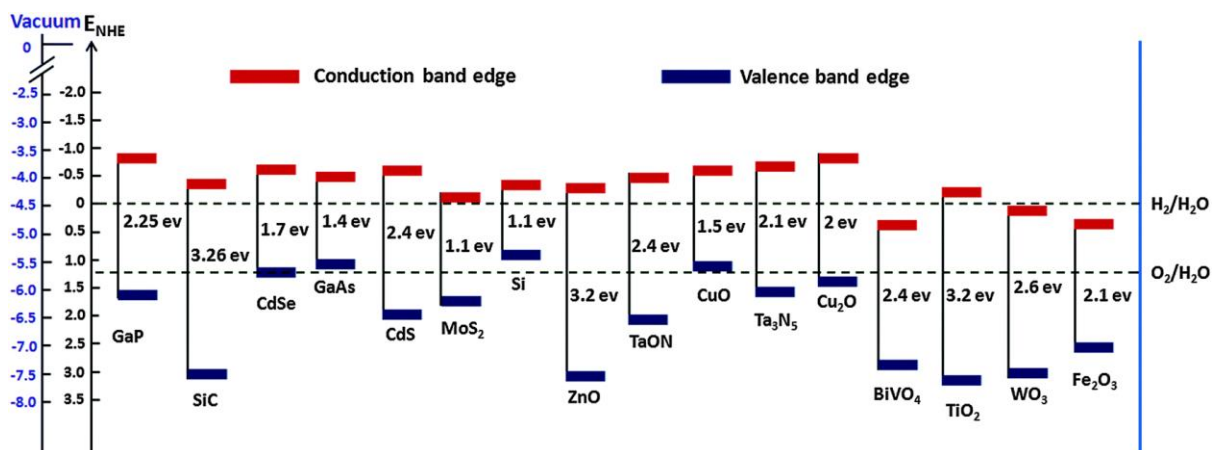


Figure 1.3. Band positions of photoactive materials and their redox potentials for water splitting in water under visible light illumination at pH = 0. Adapted from ref.[35]

Bismuth vanadate (BiVO_4) is a promising *n*-type semiconductor material that has gained considerable attention in the field of photo-electrocatalysis. Photo-electrocatalysis is a process that utilizes light to drive electrochemical reactions, such as water splitting or pollutant degradation, on the surface of a photocatalyst. Here are some key effects of bismuth vanadate on the photo-electrocatalysis.

- (i) **Visible light absorption:** The BiVO_4 has a narrow bandgap (around 2.4 eV), which allows it to absorb visible light efficiently. This property is essential for utilizing solar energy effectively, as a significant portion of solar radiation lies in the visible light range.[36]
- (ii) **Efficient charge carrier separation:** One of the critical factors for PEC efficiency is the rapid and efficient separation of photogenerated charge carriers (electron-hole pairs).[36, 37] The BiVO_4 's unique crystal structure and electronic properties facilitate the separation of these charge carriers, minimizing their recombination, and increasing the overall photocatalytic activity.
- (iii) **Favorable band positions:** The BiVO_4 exhibits suitable band positions for promoting redox reactions.[38] The position of its valence band allows for effective

oxidation processes, making it suitable for applications such as water oxidation in water-splitting reaction.

(iv) Oxygen evolution reaction (OER) catalysis: modified BiVO_4 is particularly effective for the oxygen evolution reaction, which is a key component of water splitting to produce oxygen and hydrogen.[39] Its catalytic activity in the OER makes it a promising material for photoelectrochemical water-splitting applications.

(v) Tunability: The properties of BiVO_4 can be tuned by doping with other elements or by altering its crystal structure, leading to enhanced PEC performance. Doping can adjust the bandgap, band positions, and charge carrier dynamics to optimize the material for specific applications.[40]

The BiVO_4 photoanode, while promising for photoelectrochemical (PEC) water splitting, has several limitations that can impact its overall performance such as

(i) Short-hole Diffusion Length: BiVO_4 has a short-hole diffusion length, in the range of 45-70 nm which restricts the effective separation and transport of photo-generated charge carriers, leading to recombination and reduced photocurrent.[41]

(ii) Slow Charge Carrier Dynamics: The sluggish charge carrier dynamics, especially the slow rate of hole transport, can hinder the efficient extraction and utilization of photo-generated charges.[42]

(iii) Insufficient Photocatalytic Activity: While BiVO_4 can perform water oxidation, its inherent photocatalytic activity for oxygen evolution is moderate, necessitating the incorporation of efficient co-catalysts to enhance its performance.[43]

(iv) Surface and Interface Issues: The BiVO_4 surface can exhibit surface states and defects that can trap charge carriers and lead to recombination. Proper surface engineering is essential to mitigate these issues.[44]

(v) Stability and Corrosion: BiVO_4 can undergo photo-corrosion under prolonged exposure to aggressive electrochemical conditions, leading to the degradation of the material over time.[45]

Researchers continue to explore various modification strategies such as nanostructuring, facet/texture engineering (001 facets)[46], doping[47], surface passivation [48], heterojunction formation[49], deposition of electrocatalysts (FeOOH [50], $\text{FeOOH}/\text{NiOOH}$ [51], Co-Pi [52]), have been employed to overcome these limitations and enhance the efficiency of BiVO_4 photoanode and make it more viable for real-world applications in solar fuel generation and environmental remediation. Some of the surface, bulk, and interface engineering strategies of the BiVO_4 for solar water oxidation are presented in Figure 1.4 and some of strategies are discussed in next section.

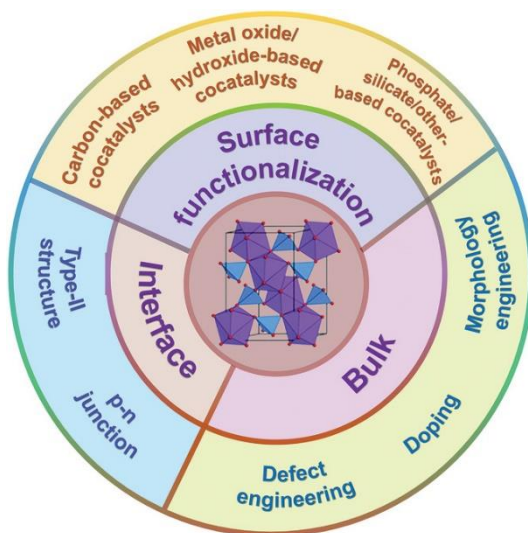


Figure 1.4. Surface, bulk, and interface engineering strategies of the BiVO_4 for solar water oxidation. Adapted from ref.[53]

1.2. Literature Review

The PEC water splitting was initially accomplished by Fujishima and Honda in the early 1970s using TiO_2 at 0.8 V with ultraviolet light.[54] The wide bandgap of TiO_2 (i.e. 3.2 eV) prevented it from being used in practical water-splitting applications. Because of this, there is now a great deal of interest in the quest for PEC photoelectrodes that are commercially viable. In recent years, scientists have successfully harvested visible sunlight using several photoelectrode materials to split water into chemical fuel (H_2). Numerous metal oxide photoelectrodes have been studied for PEC water splitting, including Fe_2O_3 [26], BiVO_4 [28], TiO_2 [30], WO_3 [31], ZnO [32], CuO [33], and C_3N_4 [55]. Among these semiconducting materials, BiVO_4 is regarded as a highly promising photoanodes because to its various advantageous characteristics. These include its non-toxic nature, abundance in the Earth's crust, low valence band position, and excellent stability in aqueous solutions. The BiVO_4 exist in monoclinic, orthorhombic, and tetragonal crystalline forms. The orthorhombic and tetragonal structures exhibit limited photoactivity because of their

symmetric symmetry. The only crystalline form (Monoclinic) of BiVO_4 exhibits an absorption capacity of around 30% towards solar radiation. This leads to a potential photocurrent density of 7.5 mA cm^{-2} , which corresponds to a solar-to-hydrogen (STH) efficiency of 9.2%. Thus far, a maximum photocurrent density of 6.72 mA cm^{-2} at $1.23 \text{ V}_{\text{RHE}}$ has been documented for the $\text{WO}_3/\text{BiVO}_4/\text{Co-Pi}$ photoanode system, which represents almost 90% of its theoretical value. Nevertheless, the STH efficiency of this system remains significantly lower than its theoretical efficiency. The observed variation in performance can be attributed to the dissipation of energy caused by the swift recombination of photogenerated charge carriers occurring at the surface and bulk of BiVO_4 , as well as at the interface between BiVO_4 and the substrate Figure 1.5a shows the yearly number of publications by using BiVO_4 for PEC water splitting. Figure 1.5b illustrates the historical improvements in photocurrent of BiVO_4 at $1.23 \text{ V}_{\text{RHE}}$ under standard illumination conditions.

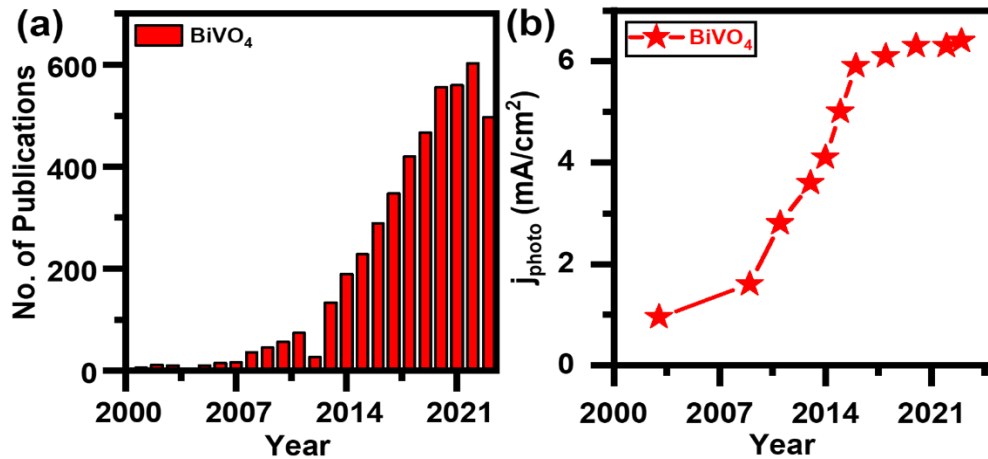


Figure 1.5. (a) Yearly number of publications by using photoelectrochemical water splitting and BiVO_4 , data extracted from Scopus (02/08/2023), and (b) Historical improvement in the photocurrent of BiVO_4 at standard conditions (1 sun and $1.23 \text{ V}_{\text{RHE}}$). Reported from ref.[56-58]

1.2.1. Surface modification with Oxygen Evolution Catalyst

One approach involves the surface's modification of the BiVO_4 photoanode would enhance the charge separation and transfer efficiency at the semiconductor electrolyte interface (SEI). It passivates the surface states and blocks the pinholes commonly encountered on the surface of BiVO_4 films. In particular, the modification with an oxygen evolution catalyst (OEC) overlayer can effectively minimize the surface recombination of charge carriers and improve the charge transfer kinetics at the SEI. Metal oxide (NiFeO_x , Co_3O_4 , MoO_x)[59-61], oxyhydroxides (FeOOH , NiOOH , CoOOH)[50, 62, 63], layered double hydroxide (LDH)[64], Co-Pi are utilized to reach this ultimate goal.[51] Recently, transition metal oxyhydroxides, e.g., FeOOH , NiOOH , CoOOH , and other layered double hydroxides (LDHs) were used to improve the kinetics of oxygen evolution reaction (OER).[51] LDHs are attractive oxygen evolution co-catalysts (OEC) due to their large surface area, and thus more active sites are available for water oxidation. The LDHs are extensively used on the surface of BiVO_4 to enhance the catalytic process of water oxidation.[65, 66] Among various reports on LDHs/ BiVO_4 photoanodes, cobalt-based LDHs showed a higher capability to passivate the BiVO_4 surface.[67] Zhao et al. electrodeposited CoMn-LDH on BiVO_4 photoanode to suppress the recombination and enhance the holes injection at the semiconductor electrolyte interface (SEI).[68] Yue et al. used plasma treatment to introduce surface defects and improve the hydrophilic nature of the CoAl-LDH/BiVO_4 photoanode to enhance charge separation and charge injection efficiency.[65] Bai et al. used CoNi-LDH OEC decorated on the BiVO_4/CdS electrode to get a ternary photoanode structure and achieved 2.72 mA cm^{-2} at $1.23 \text{ V}_{\text{RHE}}$. [69]

1.2.2. Introduction of hole transport layer on BiVO₄

The charge transfer and separation efficiencies can be regulated by using a hole transport layer (HTL) and/or hole storage layer (HSL) at the surface of semiconductor materials to improve the PEC performance.[70, 71] For instance, introducing ferrihydrite as an HTL protects the photo-corrosion of the Ta₃N₅ electrode.[72] The PEC performance of WO₃ was improved by the addition of boron nitride as HTL.[70] The interfacial layer of phosphorene as HTL was incorporated between the BiVO₄ and NiOOH OEC to boost the PEC performance of the BiVO₄ photoanode.[71] Inspired by the HTL effect on different photoanode materials, it is desirable to explore the role of 2D HTLs at the BiVO₄ surface to improve its PEC activity for the water oxidation process. Commonly, 2D graphene was introduced as HTLs to enhance the PEC performance owing to its unique electronic properties.[72] Recently, metal carbides, nitrides, or carbonitrides (MXene) were considered an emerging class of 2D materials with great potential in the field of photocatalysis and photo-electrochemistry as HTLs.[73, 74] Due to its excellent conductivity, it has the potential to increase electron transport and eventually charge separation efficiency. Furthermore, the functional groups on the surface of MXene can encourage the creation of intimate contact surfaces between it and other semiconductors, which not only improves photogenerated charge carrier separation but also assists in reactant adsorption.[73] Moreover, the work function of Ti₃C₂T_xMXene is higher than BiVO₄ which strengthens the built-in electric field at the Ti₃C₂T_x/BiVO₄ junction, which facilitates the extraction of photoexcited holes from the valance band of BiVO₄ to the MXene.[75] Yu et al. coupled TiO₂ nanorods with Ti₃C₂ MXene nanoparticles to form a heterostructure to enhance the PEC performance for the water oxidation process.[76] Ye

et al. prepared MXene/hematite Nanorod heterostructure by passivating the hematite surface with the MXene layer to improve the surface charge separation and PEC performance for water oxidation and stability.[77] Li et al. fabricated $\text{Ti}_3\text{C}_2\text{T}_x/\text{BiVO}_4$ composite through electrostatic interaction between $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets and BiVO_4 . The $\text{Ti}_3\text{C}_2\text{T}_x/\text{BiVO}_4$ composite exhibits excellent charge carrier separation and transfer due to the formation of 2D/2D heterojunction with a larger interface contact area.[78] Bai et al. loaded the Ferrihydrite MXene (Fh-MXene) layer on BiVO_4 . It was observed from the PEC analysis and DFT calculations that the Fh-MXene acts as a hole transport layer (HTL) which significantly improves the band alignment of the Fh-MXene/ BiVO_4 interface by tuning work function, which strengthens the built-in electric field for more efficient hole extraction.[79] Xie et al. grafted MXene nanosheets on ZnO nanorods for enhanced PEC water splitting. MXene constructs a heterojunction with ZnO nanorods to suppress the recombination of charges and efficiently enhance charge separation efficiency.[80] Likewise, Yang et al. designed a charge transfer system by inserting $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets between hematite (Fe_2O_3) and the oxygen evolution co-catalyst Co-Pi. It was incurred from the results that the MXene acts as a hole transport layer, which efficiently enhances the mobility of the holes, and suppresses the interfacial charge recombination.[81] Nguyen et al. synthesized $\text{Ti}_3\text{C}_2\text{T}_x$ MXene@C nanodots and deposited on the surface of molybdenum-doped bismuth vanadate (Mo- BiVO_4) as a co-catalyst for the photoanode to enhance the oxygen evolution reaction (OER). This incorporation results in a remarkable 1.5-fold increase in photocurrent density compared to pristine Mo- BiVO_4 at a potential of 1.23 V_{RHE} . This improvement can be attributed to

the enhanced light absorption and enhanced charge transfer efficiency facilitated by the $\text{Ti}_3\text{C}_2\text{T}_x\text{MXene}@C$ nanodots.[82]

Table 1.1. PEC performance of various recently reported $\text{Ti}_3\text{C}_2\text{T}_x/\text{BiVO}_4$ photoanodes. (Conditions: Unless otherwise specified, all PEC measurements were carried out under standard illumination conditions (i.e. A.M 1.5 G, 100 mW cm^{-2}) with respect to V_{RHE} .)

Photoanode	Fabrication method	j_{photo} at 0.6 V_{RHE} (mA/cm^2)	Ref.
$\text{BiVO}_4@\text{Fh-MXene}$	Electrodeposition/ hydrothermal	1.75	[79]
$\text{Ti}_3\text{C}_2\text{T}_x/\text{BiVO}_4$	Electrodeposition/ spin coating	0.50	[83]
$\text{MXene-BiVO}_4\text{-FeOOH}$	Electrodeposition/ CV deposition	1.00	[75]
$\text{MX}@C/\text{BiVO}_4$	Sol-gel spin coating/ drop-casting	1.65	[82]
$\text{BiVO}_4/\text{Ti}_3\text{C}_2$	Hydrothermal/ electrostatic interaction	0.05	[78]
$\text{Br-MXene}/\text{BiVO}_4/\text{CoBi}$	Spin coating	1.80	[84]
$\text{NiFeOOH}/\text{MoO}_x/\text{MN}/\text{BiVO}_4$	Electrodeposition/ spin coating	3.10	[61]

1.2.3. Heterostructure/heterojunction formation with BiVO_4

Heterostructure construction has attracted great interest in PEC water splitting and it is regarded as one of the most promising methods to develop photoactive materials with high efficiency.[85] It can significantly improve the charge carrier migration pathway, charge separation efficiency, redox capacity[86], hole diffusion length[87], interfacial area, and optical absorption properties.[88] The formation of a rationally designed BiVO_4 heterostructure with thermodynamic and kinetic advantages is one of the breakthrough directions to fulfill the criteria of the potential application of BiVO_4 for PEC water oxidation.[89]

For instance, George et al. synthesized $ms\text{-BiVO}_4/\text{RGO}/\text{Ag}_3\text{PO}_4$ ternary heterostructured photoanode that generates 3.60 mA/cm^2 at 1.23 V_{RHE} under standard illumination

conditions which is 2.3-fold higher than pristine *m*-BiVO₄ (1.58 mA/cm²). The enhanced PEC performance was due to the improvement in the light absorption capability and the extended hole diffusion length (209 nm) relative to pristine *m*-BiVO₄. [90] Rao et al. fabricated WO₃ NW/BiVO₄ heterojunction and reached a photocurrent of 3.1 mA/cm² and 60 % incident photon-to-current conversion efficiency (IPCE) between 300-450 nm at 1.23 V_{RHE}. The enhancement in photocurrent and IPCE value was due to the enlarged hole diffusion length from 70 nm for W:BiVO₄ to 300 nm for WO₃ NW/BiVO₄ photoanode. [49] Zhu et al. prepared a Cu₂S/BiVO₄ heterojunction that generates 2.94 mA cm⁻² at 1.23 V_{RHE} under standard illumination conditions and it exhibits 1.5-fold higher efficiency at that applied potential compared to bare BiVO₄. [91] Li et al. used WO₃/BiVO₄ nanostructured-based heterojunction to enhance the photocurrent to 1.2 mA cm⁻² at 1.23 V_{RHE}. [92] Chen et al. enhanced the charge separation efficiency to reach 88% at 1.2 V_{RHE} by using SnO₂/BiVO₄ heterostructure under front-side illumination. [93] Besides the improved charge separation efficiency, still, a fast oxygen evolution reaction (OER) is still needed to enhance the PEC performance of the heterojunction-based photoanodes. The modification of photoanodes with an oxygen evolution catalyst (OEC) can significantly reduce the onset potential and enhance the charge transfer kinetics at the semiconductor electrolyte interface (SEI). Many oxygen evolution catalysts such as FeOOH [94], FeOOH/NiOOH [39], and Co-Pi [52] are used to modify the surface of BiVO₄ instead of using the expensive IrO_x and RuO_x OECs. The amorphous Co-Pi OEC as an example is known to passivate the surface states and at the same time enhance the hole transfer kinetics. It thus suppresses the charge recombination at surface states by acting as a surface passivation layer and has catalytic effects. [95]

Pan et al. fabricated a MoS₂/BiVO₄ p-n heterojunction and achieved a photocurrent of 2.72 mA/cm² at 0.6 V_{RHE}, which is 2.4-fold higher than BiVO₄ (0.79 mA/cm²). Because the MoS₂/BiVO₄ heterojunction formation enhances the diffusion length of photo-excited charge carriers as a result there is a significant decrease in the electron-hole recombination.[96] Wang et al. designed a CdIn₂S₄/BiVO₄ heterojunction and achieved a 2.68 mA/cm² photocurrent at 1.23 V_{RHE}, which is 2-fold higher than pristine BiVO₄. The enhancement in photocurrent is due to enhancement in hole diffusion length and the rapid separation of photogenerated charge carriers in the bulk. The introduction of CQDs on CdIn₂S₄/BiVO₄ heterojunction further enhances the photocurrent to 4.84 mA/cm² due to the synergetic effect of CQDs on CdIn₂S₄/BiVO₄ heterojunction.[97] Ye et al. effectively developed a synthesis method of BiOI/BiVO₄ p-n junction and achieved a 3-fold increase in PEC performance over BiVO₄. The BiOI/BiVO₄ p-n junction enhances the charge separation and transfer efficiencies and expands the light absorption range, which is the origin of this synergetic effect.[98] Murugan et al. employed the electrodeposition method to fabricate BiVO₄/CuO heterojunction. The BiVO₄/CuO heterojunction photoanode showed a 2-fold higher PEC performance than pristine BiVO₄. The enhancement in photocurrent is due to an improvement in light absorption ability in the entire UV-Vis region, as a result, more photo-induced charge carriers and reactive sites for water oxidation are generated.[99] Similarly, various types of WO₃/BiVO₄ heterostructure were designed to improve PEC water splitting. It's worth mentioning, the overall efficiency of WO₃/BiVO₄ is much higher than that of bare WO₃ and BiVO₄. Moreover, Coelho et al. fabricated a WO₃/BiVO₄ photoanode *via* a novel electrodeposition approach. As prepared

WO₃/BiVO₄ photoanode unveiled a photocurrent density 35 and 23 times higher than pure BiVO₄ and WO₃ respectively.[100]

Table 1.2. PEC performance of benchmark BiVO₄-based heterostructure photoanodes. (Conditions: Unless otherwise specified, all PEC measurements were carried out under standard illumination conditions (i.e. A.M 1.5 G, 100 mW cm⁻²).

Photoelectrode	Electrode fabrication method	Current density (mA/cm ²) at 1.23 V _{RHE}	Stability (hrs.)	Year	Ref.
PTh/BiVO ₄	Electrodeposition	4.72	50 at 0.8 V	2024	[101]
CoPi/BiVO ₄ /WO ₃	Vacuum and Plasma Soft-Template Synthesis	4.30	3	2023	[102]
Co-Pi/Cu ₂ O/BiVO ₄	Electrodeposition	1.97	10	2023	[103]
TANF/BiVO ₄ /In ₂ O ₃	Electrodeposition	4.20	4	2023	[104]
FOOH/CQDs/CdIn ₂ S ₄ /BiVO ₄	Electrodeposition	4.99	5	2022	[97]
NiOOH/BiVO ₄ /WO ₃	Sole-gel/electrodeposition	3.00	10	2022	[62]
CuO/BiVO ₄	Electrodeposition	2.05	2	2022	[99]
NiFeO _x -HT-BiVO ₄	Electrodeposition	3.37	12	2022	[105]
NiCo-LDH/CuPc/BiVO ₄	Electrodeposition	4.03	15	2022	[106]
Cobaloxime/Ni-OEC/BiVO ₄	Electrodeposition	5.10	1	2022	[107]
Co:BiVO ₄	Electrodeposition	4.45	0.5	2022	[108]
MoO _x @2%Mo-BiVO ₄	Dip coating	1.00	18 at 0.6 V	2022	[109]
Co-Bi/Bi _{1-x} VO ₄	Spin coating	4.5	30	2021	[110]
CoFe-NiOOH/BiVO ₄	Coating by Lifting method	1.54	2	2021	[111]
CoFe-OH/Cu ₂ S/BiVO ₄	SILAR/electrodeposition	3.07	1	2021	[91]
CoNiO ₂ /BiVO ₄	Chemical bath deposition	1.16	2	2020	[112]
Co-Pi/NiFeOOH/BiVO ₄	Sol-gel method	2.03	2	2020	[43]
BiVO ₄ /WO ₃ /SnO ₂	Sol-gel spin coating	3.10	2	2017	[113]
Co-Pi/NiV ₂ O ₆ /BiVO ₄	Solution-processed methods	4.80	25 at 0.6 V	2024	This work

1.3. Spectroscopic Measurements:

Electrochemical impedance spectroscopy and intensity-modulated photocurrent spectroscopy have been used to investigate the kinetics and mechanism of water oxidation in photoanodes.

1.3.1. Electrochemical Impedance Spectroscopy

EIS provides detailed information on the kinetics and mechanisms of different electrochemical systems. It is extensively employed in the fields of corrosion research, semiconductor science, energy conversion and storage technologies, chemical sensing, and biosensing, as well as noninvasive diagnostics. EIS involves disturbing an electrochemical system that is in a stable state or equilibrium by applying a sinusoidal signal, either in the form of alternating current or voltage, across a wide range of frequencies. The system's response to this disturbance, measured as the sinusoidal current or voltage, is then monitored. Given that the electrochemical system being examined is a linear time-invariant system, meaning that the output signal is directly proportional to the input signal and the system's behavior remains constant over time, EIS is a technique that models the relationship between the output signal (ac current or ac voltage) and the input signal (ac voltage or ac current) across a wide range of frequencies.

The significance of EIS compared to other electrochemical methods is in its capacity to differentiate and, thus, offer a plethora of information on diverse electrical, electrochemical, and physical processes occurring in an actual electrochemical system. This assignment is quite tough due to the diverse range of processes, each with distinct time characteristics that vary from very quick to very slow. The resistance of a liquid electrolyte, the conductivities in the bulk and at the grain boundaries when using a solid polycrystalline electrolyte, the charging and discharging of the electric double layer at the interface between electrolytes, the influence of the electrode surface morphology and electrolyte composition on the capacitive behavior of the electric double layer, the kinetics of charge transfer reactions at the electrode, reactions occurring uniformly and

adsorption/desorption phenomena associated with charge transfer reactions, and mass transfer phenomena such as species diffusion to the electrode surface, all exhibit distinct time constants (τ), which measure the time behavior of each process.[114]

The impedance expression is divided into a real part and an imaginary part. When the real part (Z_{re}) is plotted on the X-axis and the imaginary part (Z_{im}) is plotted on the Y-axis, a “Nyquist Plot” is formed. Each point on the Nyquist plot is an impedance value at a frequency point, while the Z_{im} is negative. At the X-axis, impedance at the right side of the plot is conducted with low frequency, while, at the higher frequencies, their generated impedances are exerted on the left.[115]

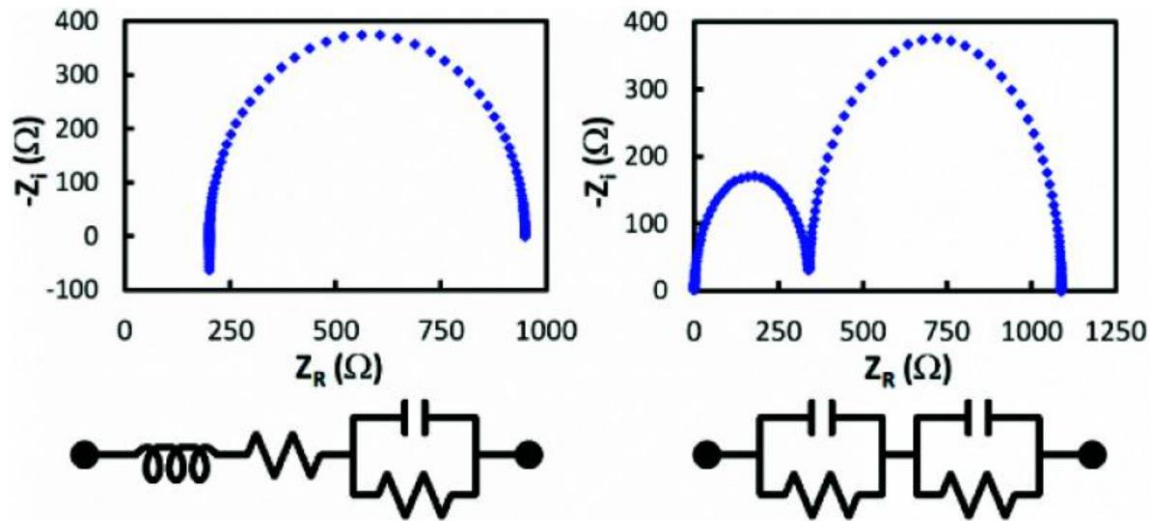


Figure 1.6. Typical EIS (Nyquist plots and their equivalent circuits). Adapted from ref.[115]

1.3.2. Intensity Modulated Photocurrent Spectroscopy (IMPS)

The IMPS involve the measurement of both the amplitude and phase shift of the photocurrent in response to the modulation of light intensity at various frequencies. The resulting amplitude values are then plotted versus frequency in a complicated diagram known as a Nyquist plot. Figure 1.7 depicts a schematic representation of the IMPS

configuration. In IMPS, the photoanode is exposed to a constant light intensity, I_0 , which is periodically varied by a tiny amplitude AC perturbation, ΔI . The I_0 is generated by applying a constant voltage through the utilization of the Autolab DAC164 module, which is coupled to the Autolab LED driver. The light modulation, ΔI , is achieved by applying a modulated voltage using the frequency response analyzer (FRA), which is also linked to the LED driver. Consequently, the photoanode will provide a consistent photocurrent response, denoted as i_0 , which is influenced by a little fluctuation in current known as Δi . The IMPS response is captured by monitoring the transfer function, $H(\omega)$, through the utilization of the external inputs of the FRA module. The modulated i_{LED} is transformed into the matching luminous intensity, and then, the photogenerated hole current is obtained by calibrating the LED using a standard Si photodiode.[116]

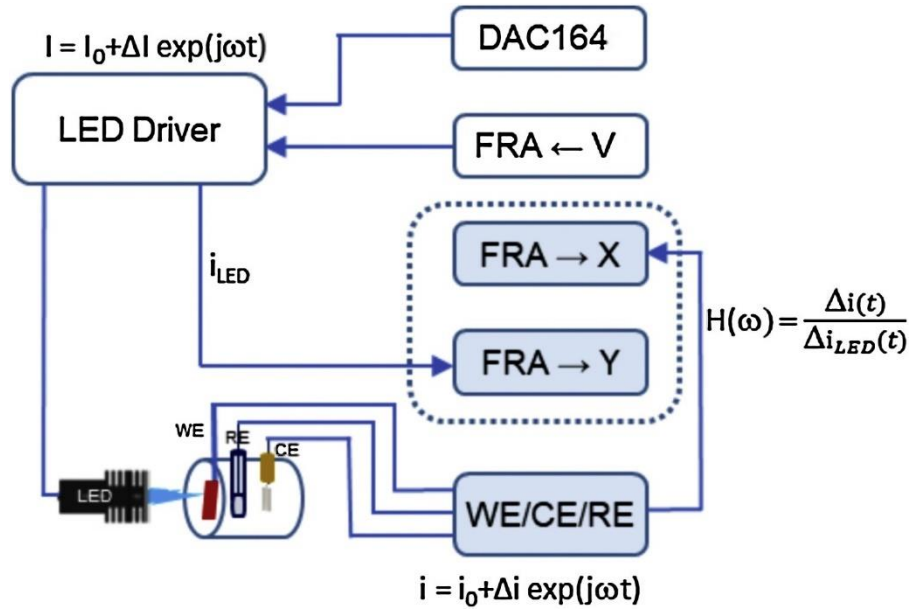


Figure 1.7. Schematic illustration of the IMPS setup. Adapted from ref.[116]

In an n-type semiconductor, the modulated light will cause a corresponding variation in the flow of positively charged particles (holes) towards the surface, known as Gärtner flux (g). These holes can either recombine with the photogenerated electrons at the surface or

undergo a reaction with adsorbed water and move to the electrolyte. Consequently, the IMPS responses consist of two separate currents. The first current is linked to the holes formed by light, while the second current is related to the electrons generated by light. These electrons need to move to the surface, where they participate in a process called surface recombination. The two currents exhibit a lack of synchronization and possess opposite polarities, resulting in the frequency-dependent variation of both the phase and amplitude of the net photocurrent. Figure 1.8 shows the typical response of IMPS of photoanode. Figure 1.8 contains two semicircles; one is in the 1st quadrant and the other is in the 4th quadrant. The high frequency (HF) semicircle starts from the 4th quadrant, which represents the attenuation time constant (RC) and comprises the total resistance of the cell and the combined capacitance of the space charge layer and Helmholtz layer capacitance. The charge transfer and recombination processes dominate the response in the 1st quadrant (LF semicircle). The rate constants of charge transfer (k_{tr}) and charge recombination (k_{rec}) at different potentials can be analyzed from the LF semicircles of IMPS results. The LF intercepts are related to surface charge transfer efficiency (η_{ct}) and $\eta_{ct} = I_1 = k_{tr}/(k_{tr} + k_{rec})$, whereas $\omega_{max} = 2\pi f_{max} = k_{tr} + k_{rec}$. [117]

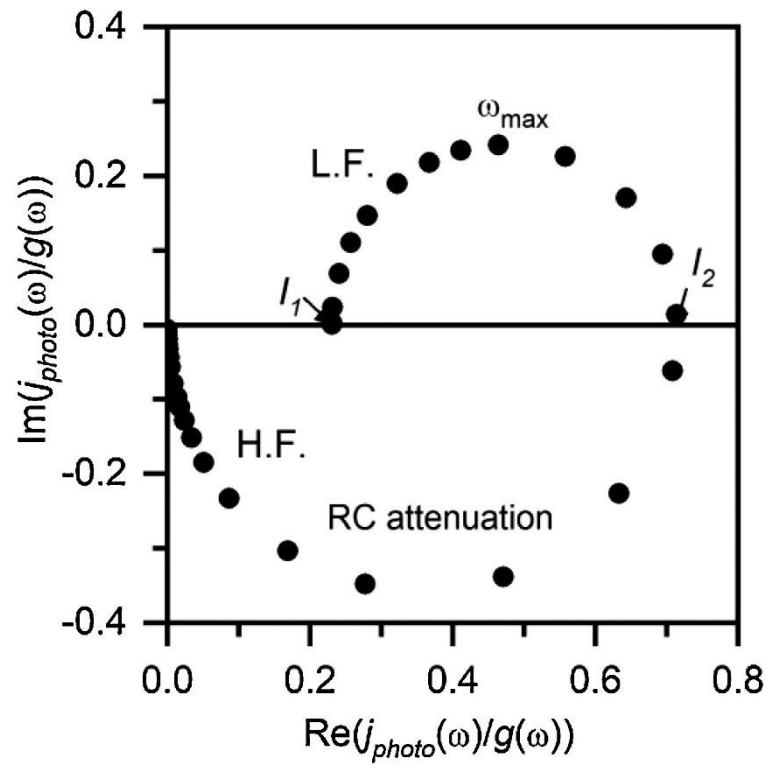


Figure 1.8. Typical IMPS response of a photoanode. Adapted from ref.[116]

1.4. Aim of Work

Based on the previous reports, it is apparent that nanostructured vanadate-based metal oxide photoanodes were tested for PEC hydrogen production. However, research is still needed to fill the gap between the current status and the ideal photocurrent expected from the BiVO_4 . Thus, this dissertation's work aims to focus on the fabrication of nanostructured vanadate-based metal oxide photoanodes. Surface passivation with MXene and modification with oxygen evolution co-catalyst will also be tested. Moreover, more focus will be given to understanding the kinetics of charge transfer and recombination before and after the alloying of BiVO_4 with transition metals (Ni and Co) to enhance the photo-induced charge carrier properties in the bulk of BiVO_4 .

2 CHAPTER TWO

MATERIALS AND CHARACTERIZATIONS

This chapter outlines the materials and the experimental methods employed throughout the thesis, which include:

- 1) The comprehensive synthetic procedure employed during the preparation and surface modification of bismuth vanadate (BiVO_4) photoanodes.
- 2) Main techniques utilized to characterize the photoanodes.
- 3) The photoelectrochemical and spectroscopic techniques employed to evaluate the PEC performance and charge transfer dynamics.

2.1. Chemicals and Glass

All chemicals used in this study were purchased from Sigma Aldrich and used without further purification. The BiVO_4 and other modified photoanode films were fabricated on the surface of F-doped SnO_2 -coated glass (FTO). Prior to the formation of BiVO_4 films, the FTO substrates underwent a comprehensive cleaning process involving detergent washing, followed by sequential sonication in deionized water, acetone, and ethanol for a duration of 10-15 minutes per stage. After that, all FTOs were stored in 2-propanol.

2.2. Synthesis methodologies

2.2.1. Synthesis of pristine BiVO_4 photoanode (chemical bath deposition method)

The BiVO_4 films were synthesized in two steps. The first step includes the fabrication of Bi_2O_3 films by the chemical bath deposition method as described in ref.[52] In a typical procedure, 2.0 mL of 0.1 M $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ dissolved in 0.8 M HNO_3 solution was taken in a beaker. Afterward, 0.5 mL of 1.0 M triethanol amine was added to the solution and stirred. Subsequently, 2.5 mL of 1.0 M KOH was added to the solution to make 5.0 mL in total and stirred for 5 min. The solution was then transferred into an auto-cleavable vial that contains FTO glass substrates and kept in the preheated oven at 50 °C for 50 min. A white layer of Bi_2O_3 was formed on the FTO surface, which was further cleaned with DI water and dried overnight at room temperature. The second step includes drop-casting 30 μL of 0.15 M vanadyl acetylacetonate (dissolved in DMSO) on the surface of Bi_2O_3 and sintering them at 450 °C for 2 h with a ramping rate of 2 °C/min. The extra content of the

V₂O₅ layer was removed from the surface of BiVO₄ films by immersing them in 1.0 M NaOH solution with gentle stirring for 5 min. Subsequently, the electrode was rinsed with water and dried.[28]

2.2.2. Synthesis of pristine BiVO₄ photoanode (drop-casting method)

The BiVO₄ photoanodes were fabricated on fluorine-doped tin oxide (FTO) by a facile and solution-processed drop-casting procedure. Briefly, 20 μ L of 0.15 M bismuth nitrate (Bi(NO₃)₃·5H₂O) and 0.15 M vanadyl acetylacetonate VO(ACAC)₂ solution (dissolved in DMSO and Bi/V atomic ratio equal to 1) was drop-cast on FTO. A geometric region measuring 0.25 cm² was confined for drop-casting the solution using heat-resistant tape. Subsequently, the FTO was kept at a hotplate and annealed at 120 °C for 2 min with a ramping rate of 5 °C/min. Consequently, after removing the tape, the electrodes were further annealed at 450 °C for 2 hours with a ramping rate of 2 °C/min. The extra layer of V₂O₅ was removed by dipping them in 1.0 M KOH solution with gentle stirring for 10-15 min and finally rinse with deionized water and dry at room temperature overnight.

2.2.3. Synthesis of Ti₃C₂T_xMXenes nanosheets

The Ti₃C₂T_x-MXenes were synthesized by following the reported method with slight modifications using a mixed acid etching technique.[118] In a typical procedure with necessary safety precautions, 1.0 g of precursor Ti₃AlC₂ MAX phase was added slowly in 10 mL mixed acid etching solutions (7.0 mL of 37% HCl and 3.0 mL of 48% HF) in 100 mL of a Teflon jar. The mixture was kept in an ice bath to cool down the contents of the jar for 10 min, and then precursor powder was added slowly to avoid the vigorous reaction and pre-oxidation of the precursor under constant stirring at 250 rpm for 20 min. Afterward,

the mixture was moved to the oil bath to maintain the uniform temperature at 35 °C with constant stirring at 400 rpm for 24 h.

The acquired product was washed and centrifuged multiple times with distilled water and ethanol (3500 rpm, 5 min/cycle) alternatively. The first supernatant was discarded to eliminate the presence of salts, dissolved residual metals, and the MAX phase. The multilayer MXenes were subjected to multiple washing cycles until the pH of the solution was neutralized to 7. The sedimented wet product was further dispersed into a 20% (Triethylamine) TEA solution at 25 °C for 4 h to delaminate the multilayered MXene into a few-layered final product. The mixture was centrifuged initially at 5000 rpm followed by multiple washing at 2500 rpm with supernatant collected until the transparent supernatant was observed. The obtained product was vacuum dried at 110 °C for 2 hours and used for further studies.

2.2.4. Modification of BiVO₄ with Ti₃C₂T_x HTL and Co-Pi Catalyst

The Ti₃C₂T_x HTL was immobilized on the BiVO₄ surface by a facile drop-casting method. The influence of the concentration (i.e., 1, 3, and 5 wt.%) and volume (i.e., 10, 20, and 30 µL) of Ti₃C₂T_x suspension on the PEC activity of BiVO₄ photoanode was investigated. Typically, 20 µL of 3 wt%Ti₃C₂T_x (2.4 mg/cm²) was drop-casted on BiVO₄ photoanode at room temperature and dried in an oven at 70 °C. The Ti₃C₂T_xMXene preparation and formation of Ti₃C₂T_x/BiVO₄ are presented in Figure 2.1.

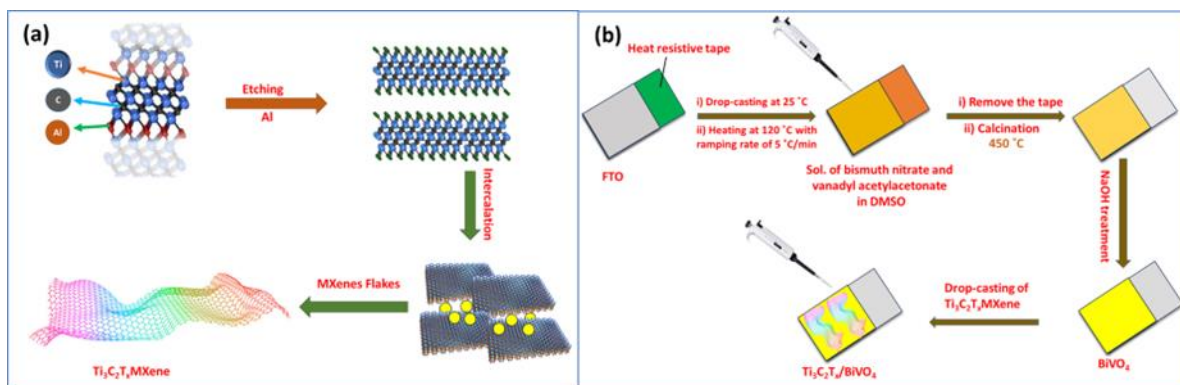


Figure 2.1. Schematic illustration for (a) the $\text{Ti}_3\text{C}_2\text{T}_x\text{MXene}$ synthesis and (b) synthesis of the BiVO_4 photoanode and drop-casting of the $\text{Ti}_3\text{C}_2\text{T}_x\text{MXene}$ on the BiVO_4 photoanode.

2.2.5. Fabrication of BiVO_4 with NiV_2O_6 BCI layer

To fabricate BiVO_4 photoanode with NiV_2O_6 BCI layer, we first deposited $\text{Ni}(\text{OH})_2$ films on cleaned FTO substrates using a chemical bath deposition method. Briefly, 5.0 mL of 0.25 M aqueous solution of nickel acetate and 0.25 M aqueous solution of hexamethylene tetramine (HMTA) were mixed and transferred into an autoclavable vial containing FTO substrates. The sealed vial is then put in an oven preheated at 90 °C and kept for 15 min, 30 min, and 45 min. The $\text{Ni}(\text{OH})_2$ films were washed with DI water and dried overnight at room temperature. Second, 20 μL of 0.15 M bismuth nitrate ($\text{Bi}(\text{NO}_3)_3$)/vanadyl acetylacetonate ($\text{VO}(\text{acac})_2$) mixture in DMSO were drop-casted on the $\text{Ni}(\text{OH})_2$ films and sintered at 450 °C for 2 hours at a ramping rate of 2 °C/min in a box furnace. The atomic ratio of Bi in the bismuth nitrate/vanadyl acetylacetonate mixture was varied between 0 to 100 at.%. The extra vanadium oxide (V_2O_5) layer formed on the top of the fabricated electrodes was removed by immersing them in 1.0 M NaOH solution for 5-10 min under a gentle string. Finally, the electrodes were thoroughly washed with DI water and dried overnight at room temperature before use. Pristine BiVO_4 films on FTO were prepared

following the same recipe without using the $\text{Ni}(\text{OH})_2$ film. The fabrication sequence of the $\text{NiV}_2\text{O}_6/\text{BiVO}_4$ photoanode is presented in Figure 2.2.

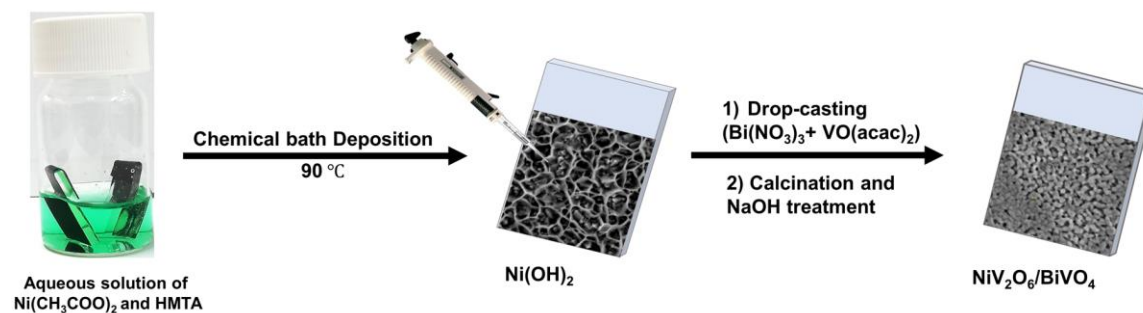


Figure 2.2. Fabrication sequence of the $\text{NiV}_2\text{O}_6/\text{BiVO}_4$ photoanode.

2.2.6. Fabrication of $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ heterostructure photoanode

The chemical bath deposition method was employed to fabricate the CoO_x layer on the FTO substrate. Briefly, 0.25 M each of cobalt acetate tetrahydrate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) and hexamethylene tetramine (HMTA) was mixed in 5.0 mL of deionized (DI) water in an autoclavable vial containing FTO. After that, put the vial in an oven at 90-95°C for 15 min, 30 min, and 45 min. The white layer of CoO_x of different thicknesses was formed due to different deposition times. In the end, the FTOs containing CoO_x layers were washed with DI water and dried in the open air for further application.

The $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ heterostructure was formed by just drop-casting 20.0 μL of different compositions of 0.15 M bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$) and 0.15 M vanadyl acetylacetonate ($\text{VO}(\text{O}_2\text{C}_5\text{H}_7)_2$) solutions in DMSO. Subsequently, these electrodes were sintered at 450 °C for 2.0 hours with a ramping rate of 2.0 °C/min in a box furnace. The extra V_2O_5 was removed by putting the $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ electrode in 1.0 M KOH solution

for 5-10 min under gentle stirring. After that, electrodes were washed with DI water and put overnight for drying.[28]

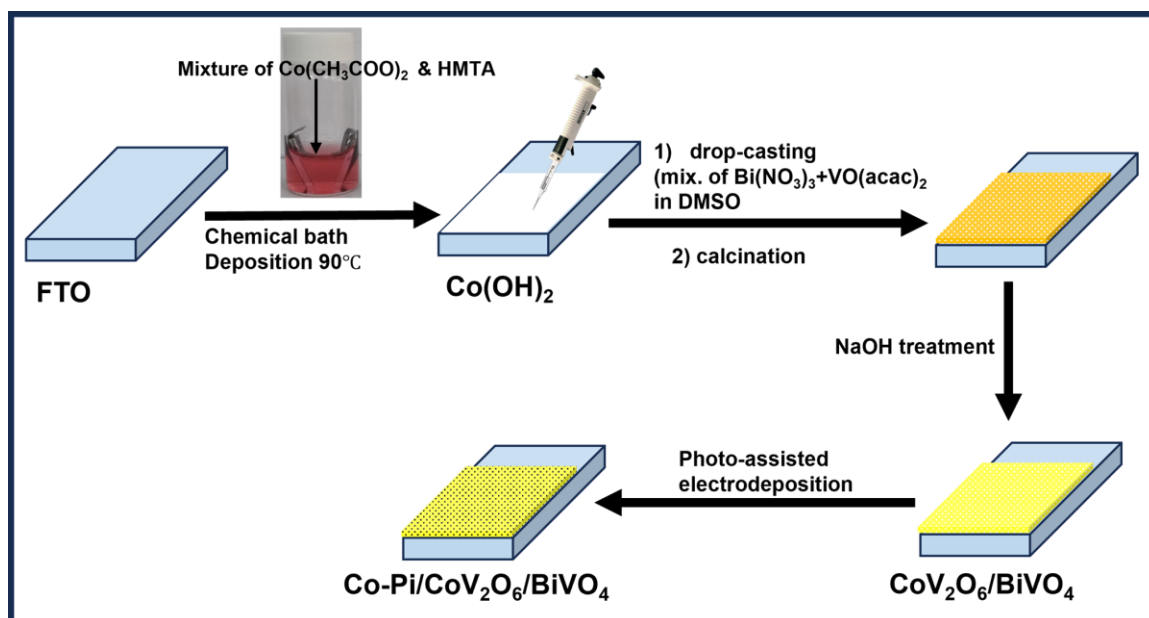


Figure 2.3. Schematic representation of Co-Pi/CoV₂O₆/BiVO₄ photoanode fabrication.

2.2.7. Electrodeposition of LDH OECs on BiVO₄ film

CoNi, CoFe, and NiFe-LDHs were electrochemically deposited on the surface of BiVO₄ photoanodes at -1.0 V vs. Ag/AgCl from a 50 mL aqueous bath saturated with N₂ gas. The deposition was stopped at 50, 100, and 150 mC cm⁻² to optimize the amount of deposited CoNi and NiFe-LDHs. In the case of CoNi-LDH, the deposition bath contained 5 mmol of Ni(NO₃)₂·6H₂O, 10 mmol of Co(NO₃)₂·6H₂O, and 3.75 mmol of NaNO₃. [69] For NiFe-LDH [66], it contains 5 mmol of Ni(NO₃)₂·6H₂O and 5 mmol of FeSO₄·7H₂O. For the deposition of CoFe-LDH [119], 0.3 mmol of Co(NO₃)₂·6H₂O and 0.3 mmol of Fe(NO₃)₃·9H₂O were used and the amount of charge (i.e. 300, 400, and 500 mC cm⁻²) was used to optimize the CoFe-LDH loading on the BiVO₄ surface. The CoNi, CoFe, and

NiFe-LDH/BiVO₄ electrodes were then rinsed with water and dried at room temperature for 5 h.

2.2.8. Fabrication of Co-Pi-Ti₃C₂T_x/BiVO₄, Co-Pi/NiV₂O₆/BiVO₄, and Co-Pi/CoV₂O₆/BiVO₄ heterostructure photoanodes

The OEC Co-Pi has been deposited on the surface of the Ti₃C₂T_x/BiVO₄, NiV₂O₆/BiVO₄, and CoV₂O₆/BiVO₄ photoanodes using a photo-assisted electrodeposition method.[52] The electrodeposition was carried out at a constant applied potential of +1.0 V vs. Ag/AgCl for 3, 5, and 7 mins. The electrolyte solution was an aqueous solution of 0.5 mM cobalt nitrate (Co(NO₃)₂·6H₂O) dissolved in 0.1 M pH 7 phosphate buffer.

2.3. Characterization

2.3.1. X-ray Diffraction (XRD)

Rigaku X-ray diffractometer with Cu K α ($\lambda = 1.54$ Å) X-ray source of radiation was for XRD measurements. The XRD pattern of all samples was recorded from $2\theta = 10^\circ - 70^\circ$ with a scan rate of $1^\circ/\text{min}$. The XRD spectrum obtained gives the relationship between light intensities vs. detector angle. During XRD measurements the distance between the sample to the detector and the sample to the X-ray focal point is the same. The sample position is fixed, and the X-ray and detector are moved simultaneously at an angle θ . The peak obtained during XRD measurements is due to the constructive interference of the diffracted wave from the sample. The intensity of the XRD peaks only depends on the number and type of scattering points in each plane.

2.3.2. Field Emission Scanning Electron Microscope (FE-SEM)

FE-SEM measurements were carried out by the TESCAN field emission microscope operating at an accelerating voltage of 15 kV. The focused beam of high-energy electrons is utilized for high-resolution images of the surface of the materials. In FE-SEM, a high-energy beam of electrons is generated and accelerated by the high voltage (1–30 kV). When this high-energy electron beam strikes the sample, it penetrates the sample for a few microns to produce different signals. The secondary and backscattered electrons are collected by the detector and combined to produce high-resolution images on the screen. For EDS measurements the LINKINCA program system was attached to the FE-SEM to find out the elemental composition of the sample. The X-ray detector is positioned in such a way that X-rays emitted by the sample are intercepted. This generates a small current which is further changed into the voltage pulse and the size of this pulse is proportional to the frequency of the X-rays.

2.3.3. X-ray Photoelectron Spectroscopy (XPS)

The X-ray photoelectron spectroscopy (XPS) examination was conducted using the ESCALAB™ Xi+ X-ray photoelectron spectrometer manufactured by Thermo Scientific. This spectrometer utilized a monochromatic micro-focused Al K α X-ray source for the XPS investigation. The calibration of the XPS spectra was performed using the C 1s peak at 284.8 eV as a reference standard.

2.3.4. Raman spectroscopy

The Raman spectroscopy analysis of the photoanodes was conducted using the HORIBA Scientific LabRAM HR Evolution Raman spectrometer. This instrument was equipped with an internal He-Ne laser emitting a red light with a power output of 17 mW and an excitation wavelength of 633 nm. A 10x objective lens was used to focus the laser on photoanode films. The acquisition time of 25 s with 2 accumulation was set for the Raman spectra collection.

2.3.5. UV-Vis Diffuse reflectance spectroscopy (UV-Vis DRS)

The Shimadzu (UV-3600i) UV-Vis-NIR spectrophotometer was used to analyze the UV-Vis diffuse reflectance spectra (DRS) of all electrodes with BaSO₄ as a reference. The bandgaps of pristine BiVO₄ and all modified photoanodes were calculated by the Tauc plots of the Kubelka-Munk function $(F(R)E)^{1/2}$ vs. Photon energy (eV).

2.3.6. Density Functional Theory (DFT) Simulations and Calculations

All DFT simulations were conducted using the Vienna ab initio simulation package (VASP)[120, 121] utilizing the projector augmented wave pseudopotentials (PAW).[122] The unit cell of BiVO₄ and NiV₂O₆ structures were optimized using gamma-entered meshes of 7 x 7 x 3 and 4 x 5 x 3, respectively to sample the Brillouin zone with the Monkhorst-Pack method.[123] To determine the electronic-level occupations, a Gaussian smearing of 0.025 eV was applied. The Perdew–Burke–Ernzerhof (PBE)[124] functional within the generalized gradient approximation (GGA) was employed to describe the exchange-correlation electron interaction energy. A cutoff energy of 520 eV and a wave

function optimization convergence criterion of 10^{-7} eV were utilized. Geometries were optimized with a force criterion of 0.03 eV/Å. Spin polarization was considered in all calculations. The DFT simulations were performed using the GGA+U formalism, which accounts for strong on-site Coulomb interactions, following Dudraev et al.'s approach.[125] This formalism includes an effective U parameter (U-J), where U represents the on-site Coulomb repulsion and J denotes the on-site Hund exchange coupling. The U parameter is set to 3.25 for V and 6.20 for Ni through all simulations. Different interfaces were built using two of the most stable facets of BiVO₄ crystal (001 and 110).

2.4. Photoelectrochemical measurements

The PEC measurements were carried out using a NOVA Autolab electrochemical workstation (PGSTAT302N) and a three-electrode configured cell adapted with a quartz window. A Verasol Oriel LSS-7120 Solar Simulator was used as a light source. The light intensity was adjusted to 1.0 sun using EKO LS-100 spectroradiometer. All the photoanodes with 0.25 cm² geometrical area were used as working electrodes, while Ag/AgCl and Pt wire were used as reference and counter electrodes, respectively. All the photoanodes were illuminated from the nonconductive (back) side of FTO and 0.5 M phosphate buffer (pH=7.0) and 1.0 M borate buffer (pH = 9) were used as an electrolyte. The measured potentials were converted to a reversible hydrogen electrode (RHE) by employing the following Nernst Eq. 2.1.[20]

$$E_{RHE} = E_{Ag/AgCl} + 0.059pH + E_{Ag/AgCl}^{\circ} \quad (2.1)$$

Where $E_{Ag/AgCl}$ is the applied potential and $E_{Ag/AgCl}^{\circ} = 0.198$ V at 25 °C.

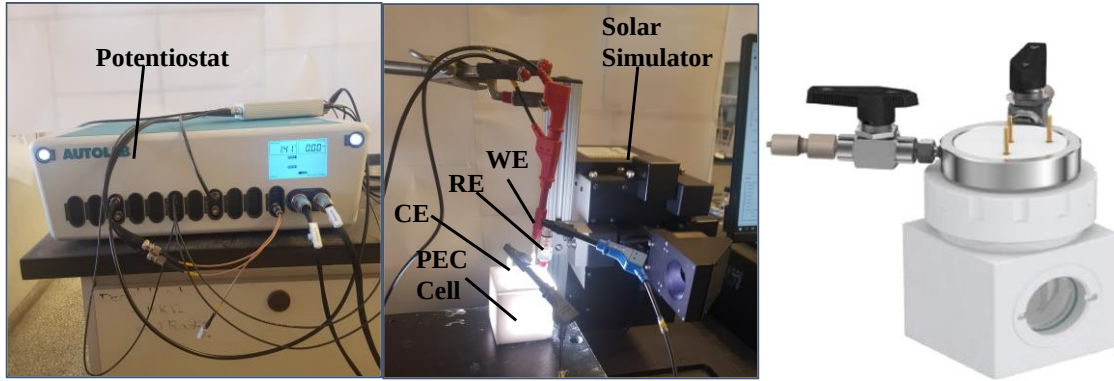


Figure 2.4. (a) NOVA PGSTAT302N potentiostat attached with (b) PEC cell under standard illumination from a solar simulator. The PEC cell has a working electrode (WE), reference electrode (RE), and counter electrode (CE) immersed in the 1.0 M borate buffer pH = 9.0, and (c) shows the sealed PEC cell to estimate the amount of H_2 and O_2 formed during PEC water splitting.

2.4.1. Linear sweep and cyclic voltammetry measurements

The three-electrode system was used during the linear sweep voltammetry (LSV) and cyclic voltammetry (CV) measurements in the dark and light to investigate the PEC activity of all photoanodes. The LSV can also be measured under chopped light, which indicates the response of the electrode under dark and light. Whereas CV can be used for the characterization of the sample by oxidation and reduction peaks of specific elements. The CV was also used to estimate the electrochemical surface area (ECSA) of the electrode.

2.4.2. Charge Separation efficiency

The separation efficiency was calculated using Eq. 2.2:

$$\eta_{sep}(\%) = \frac{j_{photo}}{j_{abs}} \quad (2.2)$$

Where j_{photo} is the photocurrent measured in 9.0 pH borate buffer and j_{abs} is the absorbed light photocurrent calculated by integrating the solar photocurrent (j_{solar}) according to Eqs.

2.3 and 2.4. The latter represents the fraction of photocurrent expected under 1.0 sun and AM1.5G illumination based on the light absorbance by the photoelectrode.

$$j_{solar} = \frac{q\lambda}{hc} I_o (1 - 10^{-A}) \quad (2.3)$$

$$j_{abs} = \int_{\lambda_1}^{\lambda_2} j_{solar}(\lambda) d\lambda \quad (2.4)$$

Where A is the absorbance, I_o is the solar irradiance ($\text{mW cm}^{-2} \text{ nm}^{-1}$) of the solar spectrum at 1.0 sun and AM 1.5G. h is the Planck's constant (J s), c is the velocity of light (nm s^{-1}), q is the electronic charge (C), λ is the wavelength (nm).

2.4.3. Chronoamperometry (CA) measurements

The CA measurements were made to evaluate the stability of the photoanodes under standard illumination conditions. The stability of the electrode was evaluated by measuring the photocurrent at specific potentials (i.e. 0.6 V_{RHE}) for modified BiVO_4 photoanodes.

2.4.4. Applied bias photocurrent efficiency (ABPE) measurements

The ABPE measurements were carried out in a two-electrode system under 1.0 sun illumination conditions. The ABPE was calculated by the following Eq. 2.5¹⁶².

$$\%ABPE = \frac{J \times (1.23 - V_b)}{P_{AM1.5}} \times 100 \quad (2.5)$$

Where J is the photocurrent density in mA/cm^2 , V_b is the applied bias vs V_{RHE} , and $P_{AM1.5}$ is light intensity 100 mW/cm^2 .

2.4.5. Incident photon-to-current conversion efficiency (IPCE) measurements

The half-cell efficiency (IPCE) was determined by measuring the chronopotentiometry responses of both pristine and modified BiVO₄ photoanodes at a voltage of 1.23 V_{RHE}. These measurements were conducted using collimated monochromatic light with varying wavelengths. The light source was a Verasol Oriel LSS-7120 Solar Simulator, which has LEDs of different wavelengths. For each wavelength, the photoanode was illuminated after 20-30 s stabilized current in the dark. The stabilized photocurrent was taken, typically 120-150 sec after illumination began. IPCE values were determined by the following Eq. 2.6.[126]

$$\text{IPCE (\%)} = \frac{(1240 \times j_p) \times 100}{\lambda \times P_{\text{light}}} \quad (2.6)$$

Where the photocurrent density (j_p) in mA cm⁻², λ is the incident light wavelength (nm), and P_{light} is the power density of incident light (mW cm⁻²), which is also measured with an EKO LS-100 spectroradiometer.

2.4.6. Photoelectrochemical impedance spectroscopy (PEIS) measurements

The PEIS measurements of photoanodes were conducted using the same electrochemical setup with a NOVA potentiostat integrated with a FRA32 M module. The Nyquist plots of all photoanodes were assessed at different applied potentials with the 100 kHz-0.1Hz frequency range with an amplitude-frequency of 10 mV under 1 sun illumination conditions.

2.4.7. Mott-Schottky (M-S) analysis

The charge carrier density (N_d) and flat-band potential (E_{fb}) of photoanodes were investigated from the M-S analysis. The acquired data was analyzed using the M-S Eq. 2.7.[127]

$$\frac{1}{C_{SC}^2} = \frac{2}{q\epsilon\epsilon_0 A^2 N_d} (E - E_{FB} - \frac{kT}{q}) \quad (2.7)$$

where C_{SC} refers to the space charge capacitance of the space charge layer in (F/cm²), A denotes the actual surface area of the electrode, measured in cm², ϵ represents the relative dielectric constant, which is 68 for BiVO₄, ϵ_0 corresponds to the permittivity of vacuum, equal to 8.85×10^{-12} N⁻¹ C² m⁻², q denotes the elementary charge, which is 1.60×10^{-19} C. N_d represents the charge carrier density, measured in cm⁻³, k signifies the Boltzmann constant, which is 1.38×10^{-23} J K⁻¹, and T represents the absolute temperature, measured in Kelvin (K). E_{fb} represents the flat-band potential, and E represents the applied potential, both measured in volts. The Mott-Schottky plots were analyzed within the frequency range of 1.0 kHz, with voltage values varying from 0.6 to 1.3 V_{RHE}, in the dark. A resistor and a capacitor were connected in series to estimate the capacitance of the C_{sc} . Under the assumption that the value of C_{sc} is significantly smaller than that of the double-layer capacitance (C_{dl}), the impact of C_{dl} on the overall capacitance is considered to be insignificant. Consequently, the capacitance computed using Eq. 2.8 can be regarded as equivalent to C_{sc} .

$$Im(Z) = \frac{-1}{2\pi fC} \quad (2.8)$$

In the above equation, $Im(Z)$ represents the complex impedance (expressed in Ohms), f denotes the frequency in Hertz, and C signifies the capacitance in Farads. Based on

equation 2.6, it is anticipated that the graph of the logarithm of the imaginary component of impedance ($Im(Z)$) plotted against the logarithm of frequency (f) will exhibit a negative slope of 1.0 in the case of pure capacitance.

2.4.8. Intensity-modulated photocurrent spectroscopy (IMPS) measurements

The IMPS responses were carried out for pristine and modified photoanodes using a PGSTAT302N workstation at various potentials with a frequency range from 0.1 Hz to 10 kHz. The modulated illumination was provided by a 470 nm Triple LED array, driven by an LED driver (Thorlabs DAC164) with an FRA 32M module attached to the workstation to perform IMPS measurements. A 10% modulation was applied over the entire frequency range.

CHAPTER THREE

RESULTS AND DISCUSSIONS

3.1. NiFe, CoNi, and CoFe-layered double hydroxides (LDH) modified BiVO₄ Photoanodes

The XRD patterns of the pristine and LDH-modified BiVO₄ photoanodes are illustrated in Figure 3.1a. The broad and weak diffraction peaks implied by the plus (+) sign and observed at 2θ equal to 24.2° , 28.8° , 42.2° , and 47.2° are well indexed to the monoclinic α -Bi₂O₃ layer formed on FTO substrate (JCPDS no. 071–0465).[128] The diffraction peaks indicated by the star (*) symbol can be well indexed for monoclinic BiVO₄ (JCPDS no. 014–0688).[50] The rest of the peaks indexed by the ($\square$) symbol belong to the FTO layer on the conductive glass substrate (JCPDS card no. 041–1445).[26] According to the reference JCPDS cards of LDHs presented in Figure 3.1a, it can be concluded that the LDH layers are beyond the detection limit, or they have an amorphous structure.[66] Figure 3.1b shows the Raman spectra of pristine and LDH-modified BiVO₄ films. The Raman peaks in the ranges of 450–460 and 520–529 cm⁻¹ correspond to the metal–OH translation mode evincing the formation of LDH assembly[129–131] rather than metal oxide. The peaks observed at around 480 cm⁻¹ in all samples belong to the FTO layer.[132, 133]

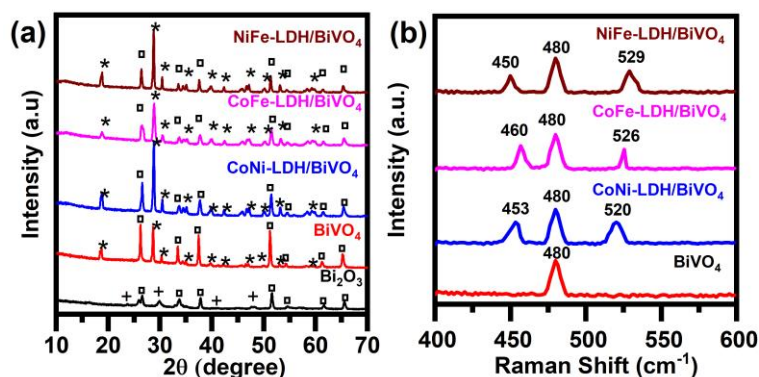


Figure 3.1. (a) XRD diffraction patterns of Bi₂O₃, pristine BiVO₄, CoNi-LDH/BiVO₄, CoFe-LDH/BiVO₄, and NiFe-LDH/BiVO₄. Plus (+), star (*) and hollow square (□) symbols indicate the Bragg diffraction peaks of Bi₂O₃, BiVO₄, and FTO, respectively. The Bragg diffraction peaks of LDHs are given as vertical lines. (b) Raman spectra of pristine BiVO₄, CoNi-LDH/BiVO₄, CoFe-LDH/BiVO₄, and NiFe-LDH/BiVO₄ respectively.

The morphologies of Bi₂O₃, pristine, and LDH-modified BiVO₄ films were examined by

SEM. Figure 3.2a shows the Bi₂O₃ film which consists of interconnected nanosheets to form a flower-like 3D structure. After heat treatment with vanadyl acetylacetonate, the

Bi₂O₃ flower-like structure is converted into worm-like BiVO₄ nanoparticles with a size of ~197 nm (Figure 3.2b). A layer of CoNi-LDH nanosheets interconnected with one another

is observed for the CoNi-LDH/BiVO₄ (Figure 3.2c). These interconnected nanosheets form a hierarchical network that maximizes the electrochemically active surface area.[134]

The SEM images of CoFe-LDH/BiVO₄ and NiFe-LDH/BiVO₄ shown in Figure 3.2d and e, respectively, indicate that the deposited CoFe and NiFe-LDH layers consist of

aggregated fine particles, and they wrap the BiVO₄ surface as it can be seen from the high-resolution SEM images presented in Figure 3.2f. Figure 3.3 shows the cyclic

voltammograms recorded in the non-faradaic region and the plots of the average capacitive current ($\Delta j/2 = (j_a - j_c)/2$ at 0.25VAg/AgCl) vs. scan rate. The slope gives the double-

layer capacitance (C_{dl}) which is directly proportional to the ECSA.[135] The ECSA of BiVO₄ < NiFe-LDH/BiVO₄ < CoFe-LDH/BiVO₄ < CoNi-LDH/BiVO₄ and the latter

exhibits 3-fold higher ECSA than that of BiVO₄. The LDH deposition on BiVO₄ enhances the ECSA and more likely the active sites for the water oxidation process.[136, 137]

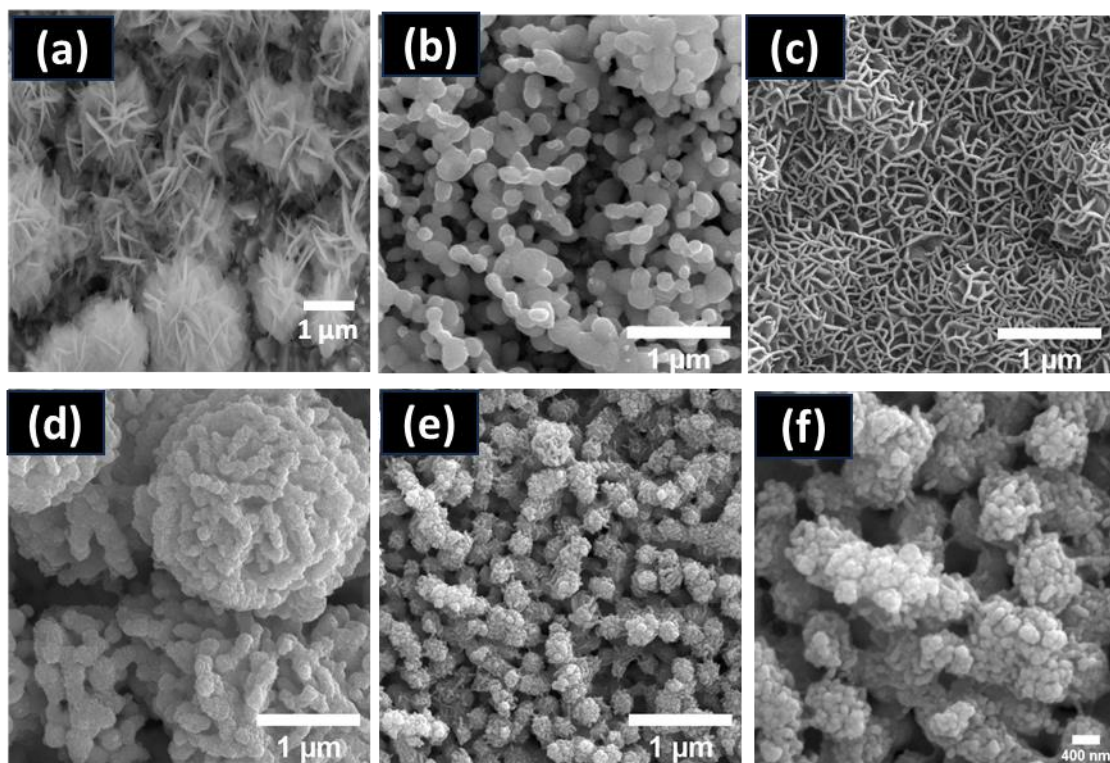
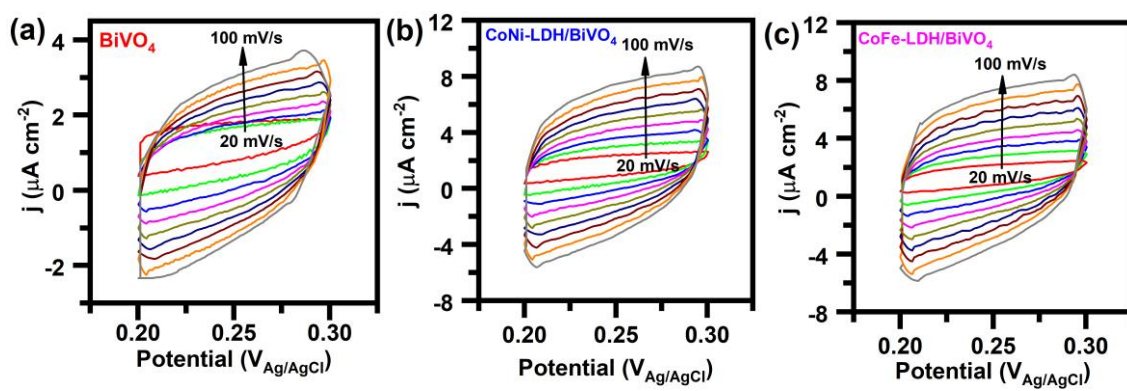


Figure 3.2. FE-SEM images of (a) Bi_2O_3 , (b) BiVO_4 , (c) CoNi-LDH/BiVO_4 , (d) CoFe-LDH/BiVO_4 , (e), and (f) low and high-resolution NiFe-LDH/BiVO_4 films.



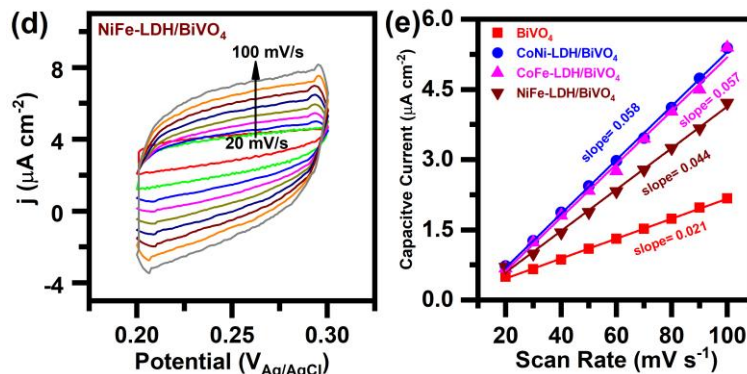


Figure 3.3. Cyclic voltammograms recorded at different scan rates (i.e., 20-100 mV s⁻¹) for (a) pristine BiVO₄, (b) CoNi-LDH/BiVO₄ (c) CoFe-LDH/BiVO₄, and (d) NiFe-LDH/BiVO₄ electrodes in the dark. Part (e) represents the plot of the average capacitive current versus scan rate.

The existence and oxidation states of Co, Ni, and Fe in the deposited LDHs were confirmed by XPS analysis. Figure 3.3a shows the XPS spectra of Ni 2p in CoNi and NiFe-LDH layers. In the CoNi-LDH, the Ni 2p core level exhibited two peaks at binding energies of 854.6 and 872.6 eV, which correspond to Ni 2p_{3/2} and Ni 2p_{1/2} peaks of Ni(II), respectively.[138] Moreover, the spin-energy separation of 17.5 eV is characteristic of Ni²⁺, which indicates the formation of α -Ni(OH)₂ phase.[139] The two satellite peaks at 859.3 and 877.7 eV further confirm that Ni is existing in the oxidation state 2+.[69] The Ni 2p_{3/2} and Ni 2p_{1/2} peaks of Ni in the NiFe LDH are shifted toward higher binding energy (i.e. 855.3 eV and 872.9 eV, respectively). This is attributed to the change in the lattice environment of Ni in the NiFe-LDH relative to that in the CoNi-LDH. Figure 3.3b shows the XPS spectra of Co in CoNi and CoFe-LDHs. The Co 2p_{3/2} and Co 2p_{1/2} peaks were observed at around 779.5 eV and 790.30 eV, respectively. The deconvolution of the Co 2p spectra indicates the presence of cobalt in the mixed oxidation states 2+ and 3+ in the CoNi-LDH.[139] Similar findings were observed for Co in the CoFe-LDH, but the XPS peak were broader and less intense and they are positively shifted due to the change in the lattice environment. The XPS spectra of Fe in the CoFe and NiFe-LDHs are shown in Figure 3.3c. The two peaks located at 710.9 eV and 724.1 eV are attributed to the Fe 2p_{3/2}

and Fe 2p_{1/2} in NiFe-LDH film, respectively.[140] The deconvolution of Fe 2p spectra indicates that Fe is present in the mixed oxidation state of Fe²⁺ and Fe³⁺ in NiFe-LDH. Similar trend is also found for Fe in the CoFe-LDH, however, the peaks were shifted towards high binding energy due to the change in the lattice environment of Fe.[141]

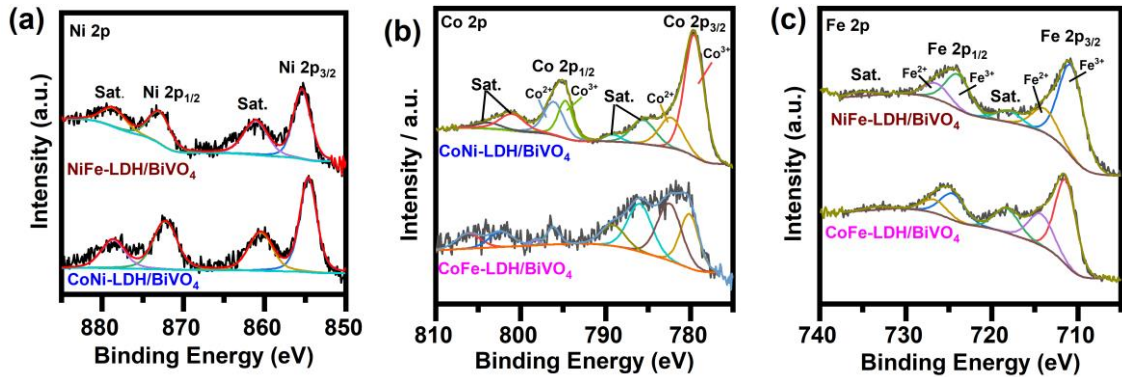


Figure 3.4. XPS core spectra of (a) Ni 2p in CoNi-LDH/BiVO₄ and NiFe-LDH/BiVO₄, (b) Co 2p spectra of CoNi-LDH/BiVO₄ and CoFe-LDH/BiVO₄, (c) Fe 2p spectra of CoFe-LDH/BiVO₄ and NiFe-LDH/BiVO₄ films. The amount of the deposited LDH electrocatalyst on BiVO₄ was controlled by applying

various amounts of charges during the electrochemical deposition. For CoNi-LDH and NiFe-LDH/BiVO₄ photoanodes, 100 mC cm⁻² was the optimum (Figure 3.5 a &b), whereas for CoFe-LDH/BiVO₄, 400 mC cm⁻² showed the best PEC activity (Figure 3.5c). Figure 3.6a shows the *I*-*V* curves of pristine BiVO₄ measured in the dark and under standard test conditions (STC) in the presence and absence of an electron donor (Na₂SO₃). Pristine BiVO₄ exhibited 0.80 mA cm⁻² at 1.23 V_{RHE} in the absence of Na₂SO₃ due to its deprived catalytic activity for water oxidation and/or surface recombination via surface states.[142] The photocurrent was significantly enhanced in presence of Na₂SO₃ and reached 2.64 mA cm⁻² at 1.23 V_{RHE}. Sulfite ions can be readily oxidized and thus the photogenerated holes that reach the surface are utilized.[143] Interestingly, almost the same photocurrent can be achieved in the absence of Na₂SO₃ after the modification of BiVO₄ with CoNi-LDH (Figure 3.6b). The CoNi-LDH/BiVO₄ exhibited 2.40 mA cm⁻² at 1.23 V_{RHE} which is 3.0-fold higher than that of pristine BiVO₄. The CoFe-LDH/BiVO₄ and

NiFe-LDH/BiVO₄ photoanodes exhibited 2.33 and 1.95 mA cm⁻² at 1.23 V_{RHE}, respectively. They showed 2.7 and 2.3-fold higher photocurrent than pristine BiVO₄, respectively. The higher PEC activity of CoNi-LDH/BiVO₄ may be attributed to the good interaction between the ultrathin nanosheets of CoNi-LDH and BiVO₄ which enhances the charge transfer efficiency and passivates the surface states of BiVO₄.^[67] The passivation effect of CoNi-LDH can be concluded also from the reduced intensity of the V⁴⁺/V⁵⁺ redox peak positioned at around 0.4 V after the deposition of CoNi-LDH (Figure 3.5d) indicating the fast transfer of photogenerated holes to CoNi-LDH layer before oxidizing V⁴⁺ to V⁵⁺.^[52] Pristine and LDH-modified BiVO₄ photoanodes exhibited excellent optical switching characteristics and fast response properties under chopped light (Figure 3.6c). The incident photon-to-current conversion efficiency (IPCE) shown in Figure 3.6d demonstrated that CoNi-LDH/BiVO₄ photoanode achieves a maximum IPCE value of 19.3 % at 375 nm, which is 5.2-fold higher than that of pristine BiVO₄ photoanode (3.7 % at 375 nm). CoFe-LDH/BiVO₄ and NiFe-LDH/BiVO₄ photoanodes showed 3.5 and 1.9-time higher IPCE than pristine BiVO₄ photoanode, respectively. Notably, CoNi-LDH/BiVO₄ photoanode showed higher IPCE than NiFe-LDH/BiVO₄ and CoFe-LDH/BiVO₄ photoanodes.

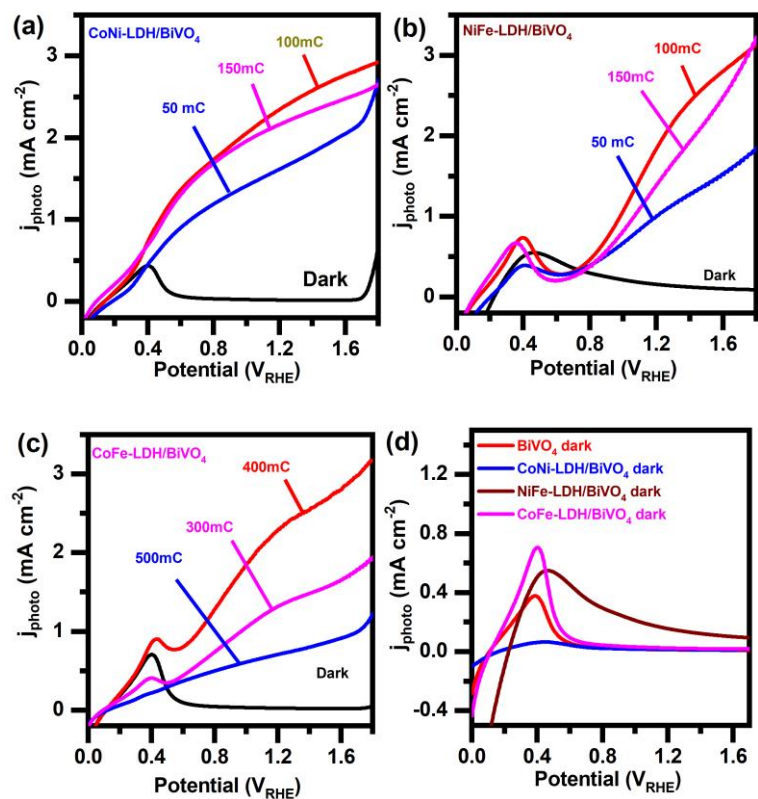


Figure 3.5. Shows I - V curves of (a) CoNi-LDH/BiVO₄, (b) NiFe-LDH/BiVO₄, and (c) CoFe-LDH/BiVO₄ fabricated at different deposition charges (i.e. 50, 100, and 150 mC cm^{-2}), (i.e. 50, 100, and 150 mC cm^{-2}), and (i.e. 300, 400, and 500 mC cm^{-2}) respectively. (d) I - V curves of pristine BiVO₄, CoNi-LDH/BiVO₄, CoFe-LDH/BiVO₄, and NiFe-LDH/BiVO₄ electrodes under dark.

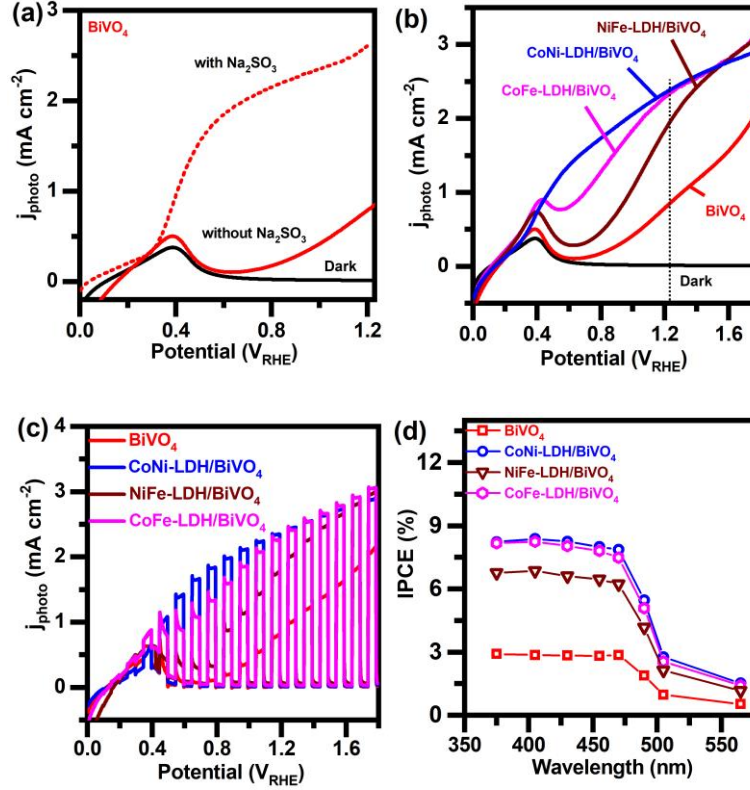


Figure 3.6. (a) j - V curves of BiVO_4 measured in 0.5 M phosphate buffer with and without Na_2SO_3 . (b) Continuous and (c) chopped light j - V curves of BiVO_4 , CoNi-LDH/BiVO_4 , NiFe-LDH/BiVO_4 , and CoFe-LDH/BiVO_4 photoanodes. (d) IPCE % of BiVO_4 , NiFe-LDH/BiVO_4 , CoFe-LDH/BiVO_4 , and CoNi-LDH/BiVO_4 photoanodes. Illumination conditions: 100 mW cm^{-2} with AM 1.5G (a, b and c) and monochromatic light (d); electrolyte: 0.5 M phosphate buffer (pH 7.0).

To explore the reason behind the high PEC activity of CoNi-LDH/BiVO_4 photoanode, the transient photocurrent (TPC) responses were measured and presented in Figure 3.7a. According to the previous reports[26, 144], the transient decay time (τ) defined as the time at which $\ln(D) = -1$ can be used to compare the lifetime of the photogenerated holes. The parameter D is determined by using Eqn. 3.1:[32]

$$D = \frac{(I_t - I_s)}{(I_m - I_s)} \quad (3.1)$$

where I_m , I_t , and I_s correspond to the photocurrent anodic spike, photocurrent at time t , and steady-state photocurrent, respectively. The τ values extracted from Figure 3.7b for BiVO_4 , NiFe-LDH/BiVO_4 , CoFe-LDH/BiVO_4 , and CoNi-LDH/BiVO_4 photoanodes are 0.26,

0.79, 2.30, and 3.80 s, respectively. These values revealed that CoNi-LDH/BiVO₄ exhibited a 15-fold enhancement in the transient decay time relative to BiVO₄ photoanode and it has the highest τ among the investigated LDHs. This indicates that the surface recombination is significantly suppressed in the presence of the CoNi-LDH layer which might act as a passivation layer. This assumption is further confirmed by measuring the generated photovoltage. Figure 3.7c shows the open circuit potential (OCP) measured under light (OCP_{light}) and dark (OCP_{dark}) for pristine and LDH-modified BiVO₄ photoanodes. The photovoltages ($\Delta\text{OCP} = \text{OCP}_{\text{light}} - \text{OCP}_{\text{dark}}$) of all the photoanodes are depicted in Figure 3.7c. A negative shift in the potential was observed under light illumination as expected for n-type semiconductors.[145] The photovoltages of CoNi-LDH/BiVO₄, CoFe-LDH/BiVO₄, and NiFe-LDH/BiVO₄ photoanodes are 0.47 V, 0.31 V, and 0.28 V, respectively. The significantly high photovoltage value of CoNi-LDH/BiVO₄ indicates that the CoNi-LDH layer indeed passivates the surface states and reduces the surface recombination better than CoFe and NiFe-LDHs. The Nyquist plots measured at 0.6 V_{RHE} under STC showed (Figure 3.7d) that the charge transfer resistance of BiVO₄ is significantly reduced after the modification with the LDHs, particularly in the case of CoNi-LDH/BiVO₄. It seems that the CoNi-LDH suppresses the charge transfer resistance and enhances the charge transfer kinetics more efficiently than CoFe and NiFe-LDHs and thus improve the water oxidation process. Subsequently, the rate of oxygen evolution reaction at the photoanode and hydrogen evolution at the counter electrode will be accelerated. To investigate this assumption, the rate constant of charge transfer and recombination was determined from the IMPS measurements.

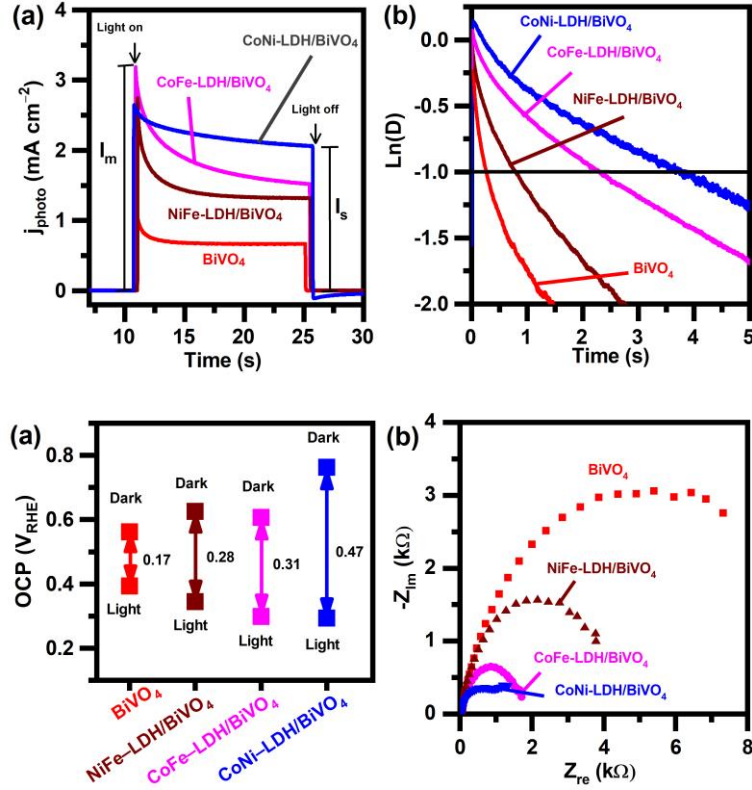


Figure 3.7. (a) Transient photocurrent (TPC) and (b) Transient decay times of BiVO₄, CoNi-LDH/BiVO₄, CoFe-LDH/BiVO₄, and NiFe-LDH/BiVO₄ photoanodes at an applied potential of 1.23 V_{RHE}, (c) Photovoltage and (d) Nyquist plots of BiVO₄, NiFe-LDH/BiVO₄, CoFe-LDH/BiVO₄, and CoNi-LDH/BiVO₄ photoanodes.

Figure 3.8(a-c) shows the typical IMPS spectra of pristine and LDH-modified BiVO₄ photoanodes. The rate constants of charge transfer (k_{tr}) and recombination (k_{rec}) were calculated from the radial frequency at the apex ($\omega_{\text{max}} = 2\pi f_{\text{max}} = k_{\text{tr}} + k_{\text{rec}}$) and the L.F. intercept $I_1 = k_{\text{tr}}/(k_{\text{tr}} + k_{\text{rec}})$ and presented in Figure 3.8(d-f).[116] It can be seen from Figure 3.8d that the order of k_{rec} is as follow: k_{rec} of NiFe-LDH/BiVO₄ > k_{rec} of BiVO₄ > k_{rec} of CoFe-LDH/BiVO₄ > k_{rec} of CoNi-LDH/BiVO₄. The latter showed the lowest recombination rate as expected from the photocurrent trend observed in Figure 3.6b. Surprisingly, the k_{tr} of NiFe-LDH/BiVO₄ is higher than that of CoNi-LDH/BiVO₄, however, it showed less PEC activity (Figure 3.8e). It seems that the kinetic of charge transfer on NiFe-LDH/BiVO₄ is superior but the surface recombination limits its overall PEC activity as evident from the short τ value. The charge transfer efficiency ($\eta_{\text{ct}} \%$ =

$(k_{tr}/(k_{tr} + k_{rec}) \times 100)$ of CoNi-LDH/BiVO₄ photoanode is still the highest (Figure 6f). From Figure 3.8a, b, and c, it is obvious that the values of the H.F. intercepts (I_2) of pristine BiVO₄, CoFe-LDH/BiVO₄, and NiFe-LDH/BiVO₄ photoanodes are almost constant at different applied potential evincing that the Fermi level is pinned and the surface passivation is not effective. However, in the case of CoNi-LDH/BiVO₄, the value of I_2 increases with increasing the applied potential (Figure 3.8a), which indicates that the CoNi-LDH layer passivates the surface states and unpin the Fermi level as schematically shown in Figure 3.9. These results fairly indicate that the high efficiency of CoNi-LDH is due to its dual characteristic functions (i.e. passivation and catalysis) and the passivation effect is important to enhance the overall efficiency. The CoNi-LDH stores the photogenerated holes via the oxidation of Co²⁺/Co³⁺ and Ni²⁺ to a higher oxidation state (i.e., Co³⁺/Co⁴⁺ and Ni³⁺/Ni⁴⁺). The high valence state species are involved in the water oxidation and the release of oxygen gas and converted back to the original Co²⁺/Co³⁺ and Ni²⁺ oxidation state. This cyclic process greatly promotes the hole transfer and effectively enhances the charge separation efficiency, which improves the sluggish water oxidation process on the BiVO₄ photoanode surface.

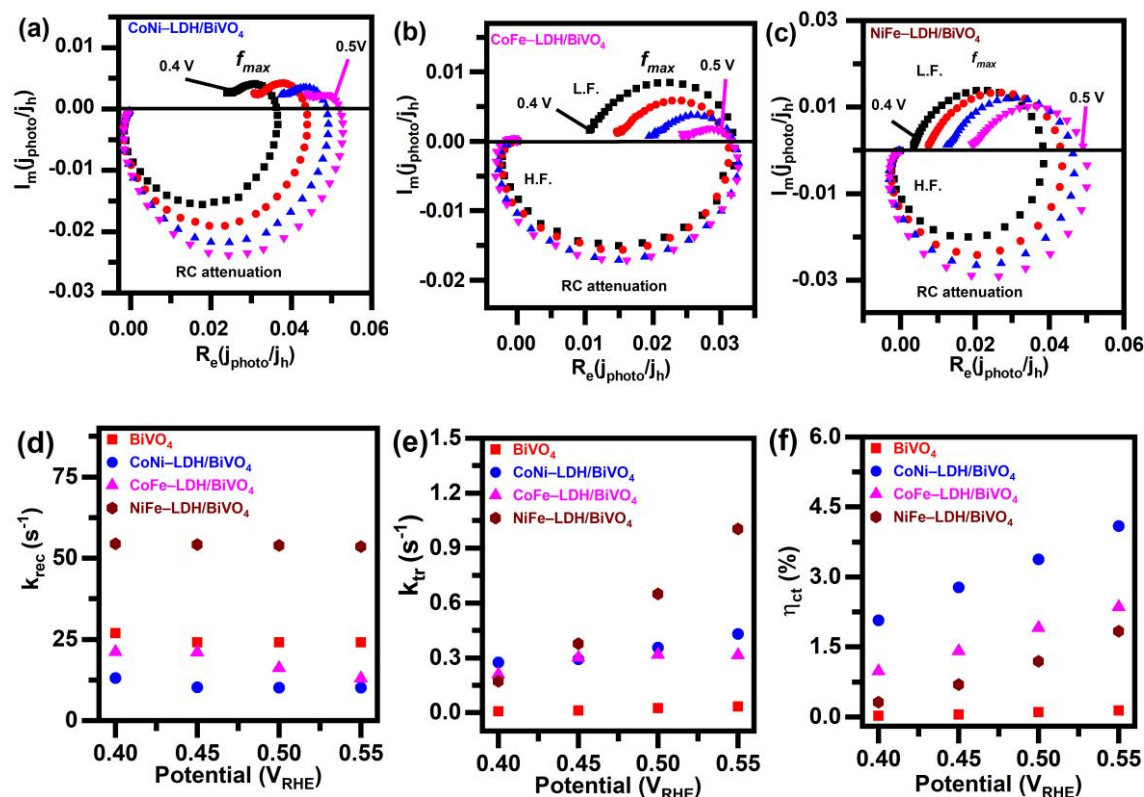


Figure 3.8. IMPS responses were measured for (a) CoNi-LDH/BiVO₄, (b) CoFe-LDH/BiVO₄, and (c) NiFe-LDH/BiVO₄ electrodes at various applied potentials in 0.5 M phosphate buffer (pH 7.0) and potential dependence of the rate constants of (d) charge recombination (k_{rec}), (e) charge transference (k_{tr}), and (f) charge transfer efficiencies (η_{ct}) of BiVO₄, CoNi-LDH/BiVO₄, CoFe-LDH/BiVO₄ and NiFe-LDH/BiVO₄ electrodes.

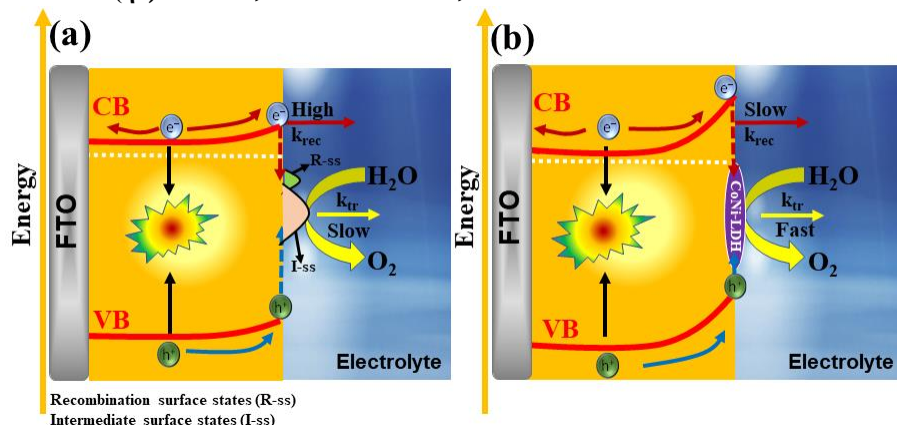


Figure 3.9. Energetic schemes for (a) BiVO₄ and (b) CoNi-LDH/BiVO₄ illustrate the charge transfer rate (k_{tr}) and surface recombination rate (k_{rec}) at BiVO₄/CoNi-LDH interfaces. R-ss and I-ss represents the recombination and intermediate surface states.

3.2. Co-Pi/Ti₃C₂T_x/BiVO₄ Photoanodes

The X-ray diffraction method was used to test the crystallinity of the prepared materials and electrodes. The X-ray patterns for Ti₃C₂T_x, BiVO₄, Ti₃C₂T_x/BiVO₄, and Co-Pi/Ti₃C₂T_x/BiVO₄ are shown in Figure 3.10a. All diffraction peaks of pristine BiVO₄ were closely matched with the JCPDS card (14-0688) evincing the formation of monoclinic BiVO₄ film on the FTO surface.[146] The XRD peaks of the FTO layer were also seen. After the loading 20 μ L of Ti₃C₂T_x suspension (3.0 wt%) by drop casting into the BiVO₄ surface, the XRD analysis was not sensitive enough to detect the diffraction peaks of Ti₃C₂T_x deposited on the surface of BiVO₄. This can be due to the low mass loading and the high dispersion of Ti₃C₂T_x within the porous BiVO₄ film. The pristine Ti₃C₂T_x MXene exhibited diffraction peaks at $2\theta = 7^\circ, 15^\circ, 27^\circ, 39^\circ$, and 58° . [147] As reported[148], the characteristic (002) peak at $2\theta=9.5^\circ$ of the MAX phase (Ti₃AlC₂) is broadened and shifted to 7° , which results from the larger d-spacing and can be explained by the structural expansion from etching and substitution of Al with -F and -OH/-O terminating groups. The most intense peak of the MAX phase at $2\theta = 39^\circ$ has nearly disappeared, confirming the removal of Al layers from Ti₃AlC₂. After loading Co-Pi onto the Ti₃C₂T_x/BiVO₄ electrode, no obvious difference in its diffraction pattern could be seen mainly due to the low amount of Co-Pi and its amorphous nature as previously reported.[149]

Raman spectra of BiVO₄, Ti₃C₂T_x, and Ti₃C₂T_x/BiVO₄ electrodes were collected to confirm the existence of the Ti₃C₂T_x on the surface of the Ti₃C₂T_x/BiVO₄ electrode (Figure 3.10b). The vibrational bands of BiVO₄ at 216, 333, 366, 701, and 830 cm^{-1} were detected, and they matched the external vibration modes and asymmetric-symmetric bending vibrations of the VO_4^{3-} ions.[150] The distinctive Raman bands located at 701 and 830 cm^{-1} are

corresponding to the asymmetric and symmetric V-O stretching modes.[151] The distinctive Raman peaks of $\text{Ti}_3\text{C}_2\text{T}_x$ at 196, 231, 336, 611, 694, 1354, and 1465 cm^{-1} are well matching for the $\text{Ti}_3\text{C}_2\text{T}_x$ reported in the literature.[152] The oxygen-terminated $\text{Ti}_3\text{C}_2\text{O}_2$'s exhibited the Ti-C and C-C vibrational peaks (A_g^1 symmetry) located peaks at 231 and 611 cm^{-1} , respectively. The O atoms' E_g vibrations are said to be responsible for the peak at 336 cm^{-1} . The C atoms in the OH-terminated MXene's E_g vibrations are mostly responsible for the peak at 611 cm^{-1} . The data shown above with less intense bands demonstrates that MXene's surface has a few surface terminations, including -OH and -O. The presence of multiple surface-terminated functional groups, which may have an impact on the phonon dispersion of MXene, is likely the cause of the blended and less intense Raman peaks. Further evidence that no titanium dioxide has developed on the surface of $\text{Ti}_3\text{C}_2\text{T}_x$ is provided by the lack of the TiO_2 characteristic peak at 144 cm^{-1} . Moreover, the two peaks observed at 1354 and 1465 cm^{-1} are characteristic of the D- and G-modes of graphitic carbon in $\text{Ti}_3\text{C}_2\text{T}_x$. [94] For the Raman bands of $\text{Ti}_3\text{C}_2\text{T}_x/\text{BiVO}_4$ photoanode, a broadening in the peaks located at 214 cm^{-1} and 333 cm^{-1} is observed due to the blending of BiVO_4 peaks with that of MXenes. Besides, after loading the $\text{Ti}_3\text{C}_2\text{T}_x$ on the surface of BiVO_4 it is observed that the most of Raman bands of $\text{Ti}_3\text{C}_2\text{T}_x$ have vanished due to the porous structure of the BiVO_4 base material. Moreover, the Raman peaks located at 1390 and 1486 cm^{-1} , which are assigned to the D and G bands of carbon in $\text{Ti}_3\text{C}_2\text{T}_x$ and do not overlap with that of BiVO_4 , indicate the existence of $\text{Ti}_3\text{C}_2\text{T}_x$ on the BiVO_4 surface.[153] The optical characteristic is a crucial parameter and has a great influence on the photoelectrode activity. In this regard, we used UV-Vis spectroscopy to explore the influence of $\text{Ti}_3\text{C}_2\text{T}_x$ loading on the optical characteristics of BiVO_4 , and the findings are

shown in Figure 3.10c. The BiVO_4 absorption edge was calculated to be at wavelengths of 511 nm.[154] The bandgap (E_g) of BiVO_4 was determined to be 2.45 eV, using the Tauc plot presented in Figure 1d.

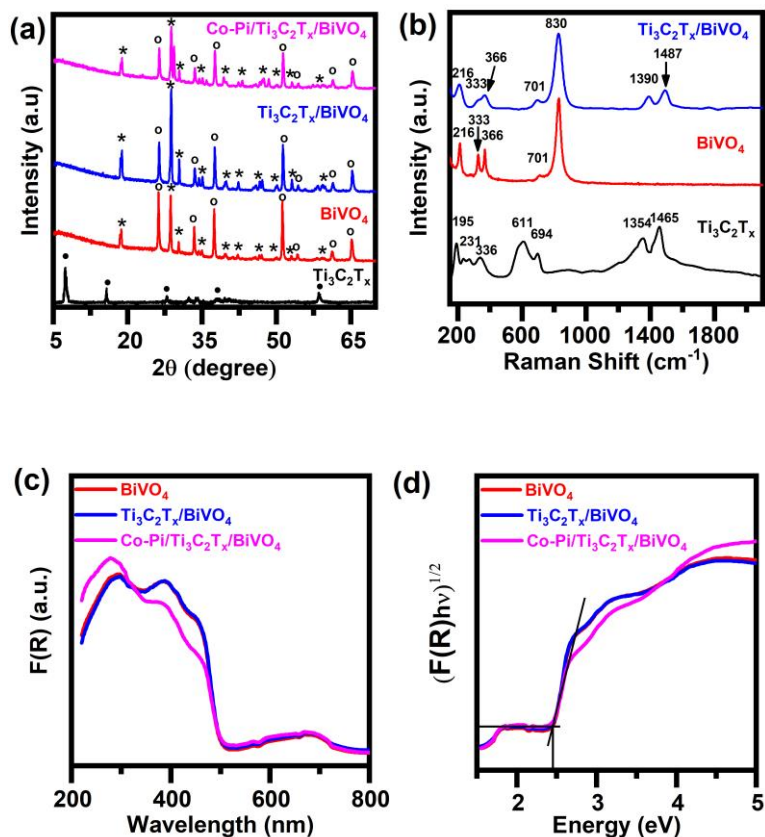


Figure 3.10. (a and b) XRD diffraction patterns and Raman spectra for $\text{Ti}_3\text{C}_2\text{T}_x\text{MXene}$, pristine BiVO_4 , $\text{Ti}_3\text{C}_2\text{T}_x/\text{BiVO}_4$, and $\text{Co-Pi/Ti}_3\text{C}_2\text{T}_x/\text{BiVO}_4$. A solid dot (•), star (*), and hollow circle (o) symbols indicate the Bragg diffraction peaks of $\text{Ti}_3\text{C}_2\text{T}_x\text{MXene}$, BiVO_4 , and FTO, respectively; (c, and d) DRS and Tauc's plots of BiVO_4 , $\text{Ti}_3\text{C}_2\text{T}_x/\text{BiVO}_4$, and $\text{Co-Pi/Ti}_3\text{C}_2\text{T}_x/\text{BiVO}_4$ photoanodes.

The UV-Vis spectra after the modification of BiVO_4 with $\text{Ti}_3\text{C}_2\text{T}_x$ and/or Co-Pi were also collected for the prepared photoanodes. There was no obvious difference in the optical properties observed except that the $\text{Co-Pi/Ti}_3\text{C}_2\text{T}_x/\text{BiVO}_4$ photoanode exhibited slightly lower absorption in the UV and visible light regions than that of parent BiVO_4 photoanodes due to the deposition of the Co-Pi layer, but the absorption onset remains the same

confirming that no change in bandgap energies after modification as shown in Figure 3.10d.[83] The Co-Pi layer on the top of BiVO₄ seems to block a little light absorption. Thus, backside illumination is used in this study.

The morphology and elemental composition of Ti₃C₂T_xMXene, BiVO₄, Ti₃C₂T_x/BiVO₄, and Co-Pi/Ti₃C₂T_x/BiVO₄ were investigated with FE-SEM, FE-TEM, and EDS, respectively. Figure 3.11a displays the FE-SEM image of Pristine BiVO₄, whereas Figure 3.11b shows the Ti₃C₂T_x/BiVO₄ Nanocomposite that depicts how BiVO₄ seems to adhere to the MXene surface. Figure 3.11b shows the morphological evolution after the drop-casting of 3% Ti₃C₂T_x; the translucent film as speculated to be of Ti₃C₂T_x attached on the surface of the BiVO₄ was observed, confirming the physical adhesion of MXenes film on the surface of BiVO₄ without affecting the morphology of the base material. The FE-SEM images of Co-Pi/Ti₃C₂T_x/BiVO₄ photoanodes are presented in Figure 3.11c. The layered structure of the Ti₃C₂T_x was further verified by the TEM technique, the nanosheets of the layered Ti₃C₂T_x can be seen in Figure 3.11d. The Ti-C-Ti stacked transparent layers observed confirm the few-layered thickness of the prepared MXenes, which is favorable for faster inter-band electronic transition.[155, 156] To create a porous network of Ti₃C₂T_x/BiVO₄ Nanocomposite, the non-uniform translucent cluster of Ti₃C₂T_x seems to combine with the BiVO₄. The TEM image indicates that Ti₃C₂T_xMXene nanosheets are well embedded in BiVO₄ film (Figure 3.11e), which facilitates the migration of photocarriers between bulk and surface.

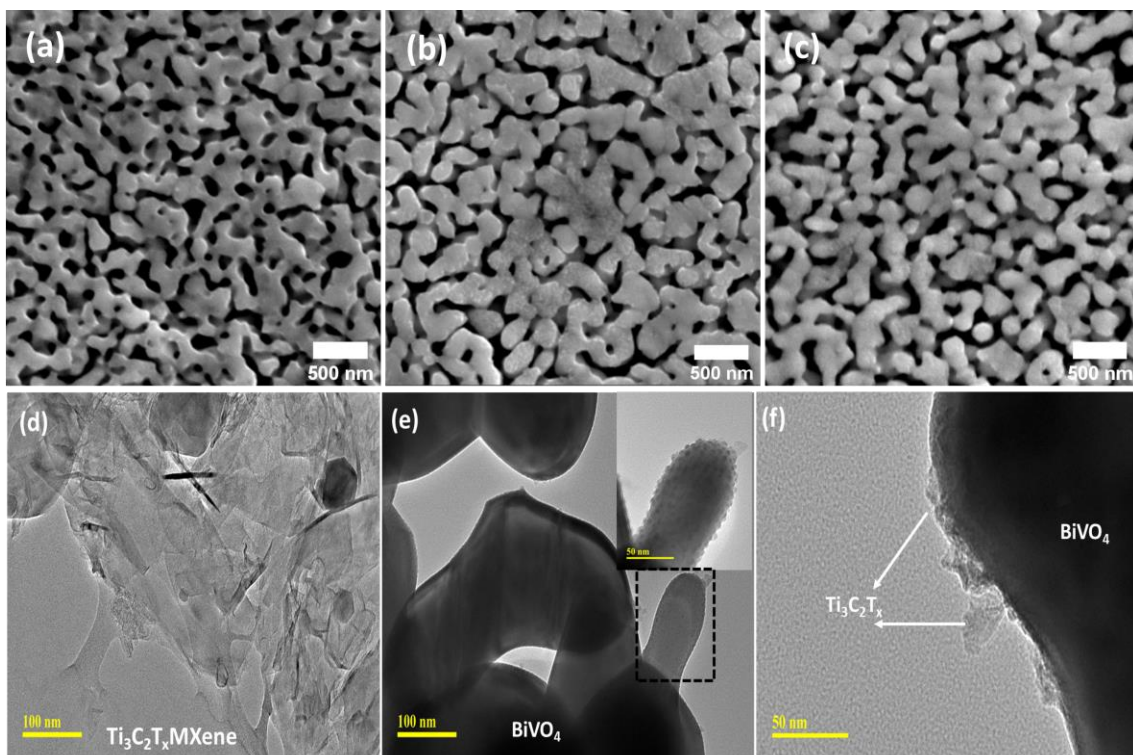


Figure 3.11. (a, b, and c) denotes the FE-SEM images of pristine BiVO₄, Ti₃C₂T_x/BiVO₄, and Co-Pi/Ti₃C₂T_x/BiVO₄ photoanodes, respectively; (d, e and f) denote the TEM images of Ti₃C₂T_x, BiVO₄, and Ti₃C₂T_x/BiVO₄, respectively.

The PEC measurements of all electrodes were measured under AM 1.5 G illumination (100 mW/cm²) in 1.0 M borate buffer (pH = 9). The electrolyte was stirred and bubbled with N₂ gas before measurements for 30 min. Firstly, Ti₃C₂T_xMXene is deposited on the BiVO₄ photoanode by drop-casting and the areal loading is optimized using linear sweep voltammetry (LSV, Figure 3.12 (a and b)). The optimized Ti₃C₂T_x/BiVO₄ photoanode (i.e. loaded with 2.4 mg/cm² of MXenes) shows a significant enhancement in photocurrent than pristine BiVO₄ in the absence and presence of a hole scavenger Na₂SO₃ as shown in Figure 3.13a. In the absence of Na₂SO₃, the pristine BiVO₄, and Ti₃C₂T_x/BiVO₄ photoanodes showed 0.45 mA/cm² and 2.31 mA/cm², respectively. But in the presence of a hole scavenger, both photoanodes showed enhanced photocurrent relative to that obtained in borate buffer (i.e. 3.20 and 5.27 mA/cm² for BiVO₄ and Ti₃C₂T_x/BiVO₄, respectively).

Sulfite ions (SO_3^{2-}) can be easily oxidized and usually, it is assumed that almost all surface photogenerated holes can be captured and reflected in the generated photocurrent in the presence of (SO_3^{2-}) ions. Based on this assumption, the maximum photocurrent expected for pristine $BiVO_4$ should be 3.20 mA/cm^2 and the loading of $Ti_3C_2T_xMXene$ film onto the $BiVO_4$ should result in a significant improvement in the photocurrent and 5.27 mA/cm^2 could be achieved. Assuming that all holes generated in the space charge layer (SCL) and the near vicinity of pristine $BiVO_4$ could diffuse and reach the surface and be collected by the sulfite ions, it can be concluded from these results that the $Ti_3C_2T_xMXene$ layer does not only reduce the surface recombination but also increase the hole collection. Figure 3.13b shows the LSVs of pristine $BiVO_4$, $Ti_3C_2T_x/BiVO_4$, and $Co-Pi/Ti_3C_2T_x/BiVO_4$ photoanodes. All photoanodes show approximately zero dark currents which indicates that there is no reaction in the dark. As expected, under light illumination, the $Co-Pi/Ti_3C_2T_xMXene/BiVO_4$ photoanode shows a higher photocurrent of 4.72 mA/cm^2 which is 2 times higher than $Ti_3C_2T_xMXene/BiVO_4$ (2.31 mA/cm^2) and approximately 11 times than that of pristine $BiVO_4$ (0.45 mA/cm^2) photoanodes. The enlarged $I-V$ curves of pristine $BiVO_4$, $Ti_3C_2T_x/BiVO_4$, and $Co-Pi/Ti_3C_2T_x/BiVO_4$ in the dark are presented in Figure 3.12d. The redox peak of V^{4+}/V^{5+} at $0.4 V_{RHE}$ was observed and significantly reduced after the deposition $Co-Pi$ on $Ti_3C_2T_x/BiVO_4$ indicating the passivation effect of $Co-Pi$ and the fast transfer of photogenerated holes to $Co-Pi$ layer before oxidizing V^{4+} to V^{5+} . [52] Figure 3.13c shows the incident photon to current efficiencies (IPCE) of all photoanodes. There is a significant enhancement in overall optical response for $Ti_3C_2T_x/BiVO_4$, and $Co-Pi/Ti_3C_2T_x/BiVO_4$ photoanodes. As described earlier there is no significant change in the absorption capability before and after loading $Ti_3C_2T_x$, and $Co-Pi/Ti_3C_2T_x$ on the $BiVO_4$

photoanode. So the enhancement of IPCE might be ascribed to the improvement of bulk carrier's transfer dynamics and surface reaction.[79] The Co-Pi/Ti₃C₂T_x/BiVO₄ photoanode shows excellent PEC stability tested by applying a constant bias potential of 0.6 V_{RHE} for 72 hours and is presented in Figure 3.13d. After 72 hours there is only a 12 % decrease in photocurrent.

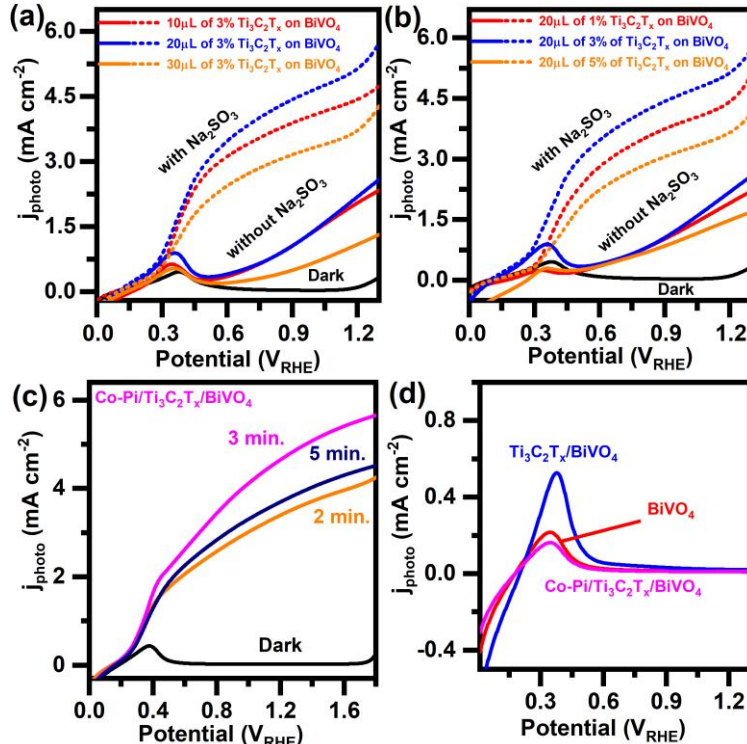


Figure 3.12. (a) LSVs of drop-casting 3% (10, 20, and 30 μL) of Ti₃C₂T_xMXene on BiVO₄ with and without Na₂SO₃ in 1.0 M (9.0 pH) borate buffer. (b) LSVs of drop-casting 20 μL (1, 3, and 5%) of Ti₃C₂T_xMXene on BiVO₄ with and without Na₂SO₃ in 1.0 M (9.0 pH) borate buffer. (c) LSVs of photoelectrochemical deposition of oxygen evolution co-catalyst Co-Pi on Ti₃C₂T_x/BiVO₄ at different time intervals. (d) LSVs of pristine BiVO₄ and the modified photoanodes under dark.

The applied bias photo-to-current (ABPE) is another evaluation metric to test the overall water-splitting reaction for pristine BiVO₄, Ti₃C₂T_x/BiVO₄, and Co-Pi/Ti₃C₂T_x/BiVO₄ photoanodes (Figure 3.13e). The Co-Pi/Ti₃C₂T_x/BiVO₄ photoanode exhibits 1.29% efficiency at 0.45 V_{RHE}, which is 2 and 8 times higher than those of Ti₃C₂T_x/BiVO₄ (0.64% at 0.47 V_{RHE}) and pristine BiVO₄ (0.16% at 0.61 V_{RHE}). It should be noticed that the bias potential corresponding to the highest efficiency value for the Ti₃C₂T_x/BiVO₄ photoanode

is shifted cathodically, indicating that the introduction of MXene reduces the carrier recombination and enhance the generated Photovoltage.[75]

To confirm that the obtained photocurrent is produced due to the water-splitting process, it is crucial to quantify the quantities of hydrogen (H_2) and oxygen (O_2) gases generated by the water-splitting process. For this, an airtight PEC cell was constructed, having a typical 3-electrodes setup of a Co-Pi/ $Ti_3C_2T_x$ /BiVO₄ photoanode, a Pt counter electrode, and an Ag/AgCl reference electrode. The PEC cell was directly connected to the gas chromatograph. Consequently, it is possible to concurrently assess the photocurrent and the concentration of the generated H_2/O_2 gases. Figure 3.13f shows the evolution of both gases and the simultaneously recorded photocurrent over time, respectively. The experiment was conducted in the 1.0 M borate buffer solution pH 9.0 at 1.23 V_{RHE} under AM1.5 simulated solar light. Figure 3.13g illustrates the Faradaic efficiency that corresponds to the ratio between the directly measured gas production rate and the photocurrent produced during the run. The photoanode achieved a faradaic efficiency of around 90-91%.

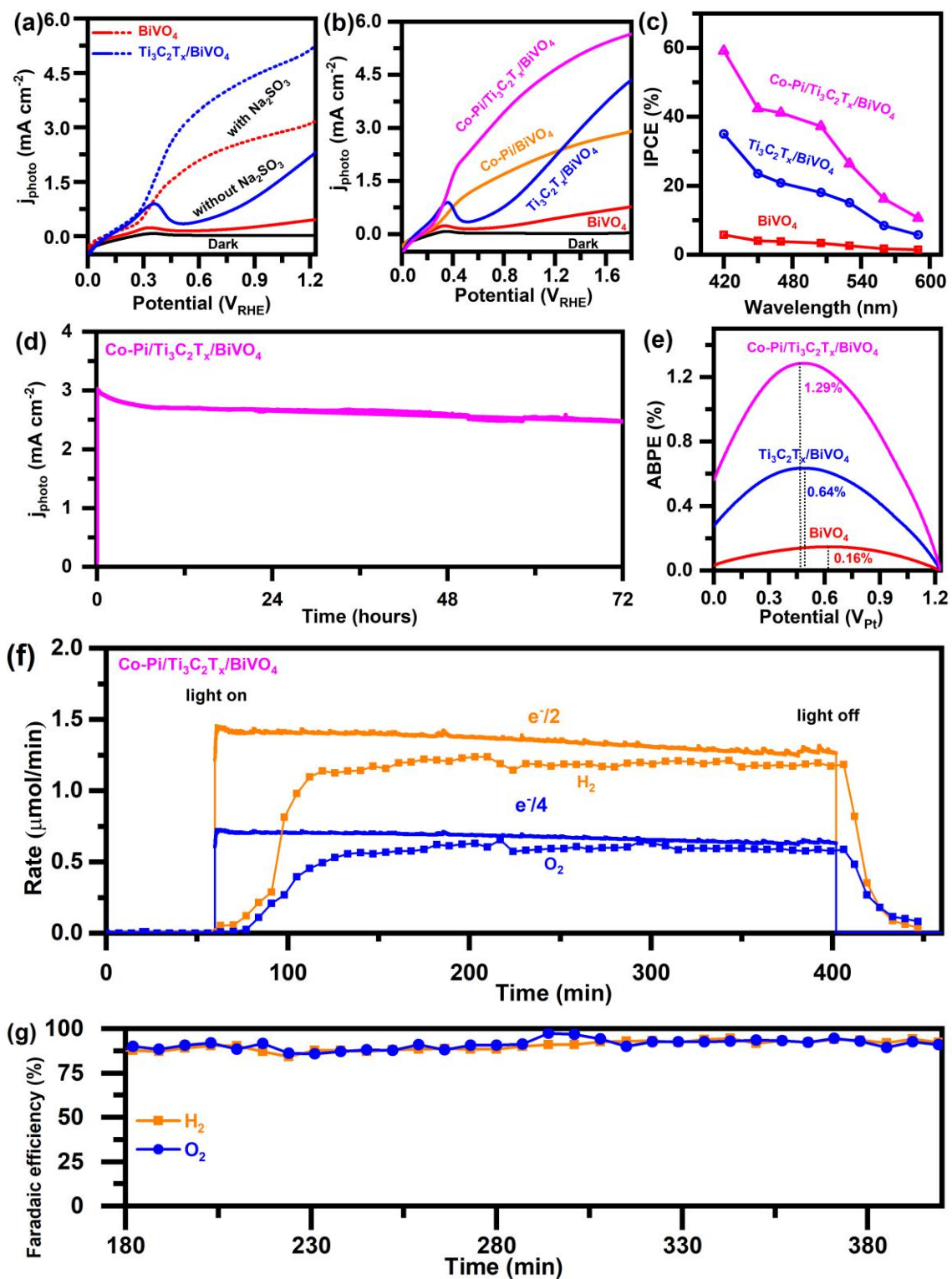


Figure 3.13. (a) I - V curves for pristine BiVO_4 and $\text{Ti}_3\text{C}_2\text{T}_x/\text{BiVO}_4$ photoanodes measured with and without Na_2SO_3 ; (b, c, and e) I - V , IPCE %, and ABPE % curves of $\text{Co-Pi}/\text{Ti}_3\text{C}_2\text{T}_x/\text{BiVO}_4$ photoanode measured without Na_2SO_3 (for clarity the curves for BiVO_4 , $\text{Co-Pi}/\text{BiVO}_4$, and $\text{Ti}_3\text{C}_2\text{T}_x/\text{BiVO}_4$ were also added); and (d) chronoamperometry stability test for $\text{Co-Pi}/\text{Ti}_3\text{C}_2\text{T}_x/\text{BiVO}_4$ photoanode measured at 0.6 V_{RHE} , (f) number of moles of H_2 and O_2 produced from the amount of photocurrent produced and from GC at 1.23 V_{RHE} in 1.0 M borate buffer solution pH 9.0, and (g) shows the respective Faradaic efficiencies of $\text{Co-Pi}/\text{Ti}_3\text{C}_2\text{T}_x/\text{BiVO}_4$

photoanode. Illumination conditions: 100 mW cm⁻² with AM 1.5 G filter except for IPCE monochromatic light of LEDs was used; electrolyte: 1.0 M borate buffer solution pH 9.0.

The EIS tests are performed to further visualize the barrier of carrier migration of all photoanodes under AM 1.5 G illuminations at 0.8 V_{RHE} as shown in Figure 3.14a. The semicircle of Nyquist plot of Ti₃C₂T_x/BiVO₄ photoanode is much smaller than pristine BiVO₄ suggesting that MXene effectively reduces the impedance for charge transfer at the electrode/electrolyte interface and as a result carrier separation and migration to the surface is enhanced. The Co-Pi further reduces the charge transfer resistance, but, still, we can conclude that the Ti₃C₂T_x MXene layer has a significant impact. Co-Pi is known to accelerate the water oxidation kinetics and improve the carrier transfer efficiency at the electrode-electrolyte interface, either by passivation and catalysis effects or by the creation of a p-n junction.[157] The open circuit potential (OCP) was examined to further explain the improvement in charge carrier separation of all photoanodes. The change in open circuit potential (Δ OCP) is shown in Figure 3.14b. From the above OCP graph, the decay lifetime (τ) of accumulated electrons can be calculated by using the model presented by Bisquert and co-workers by using the given equation 3.2.[158]

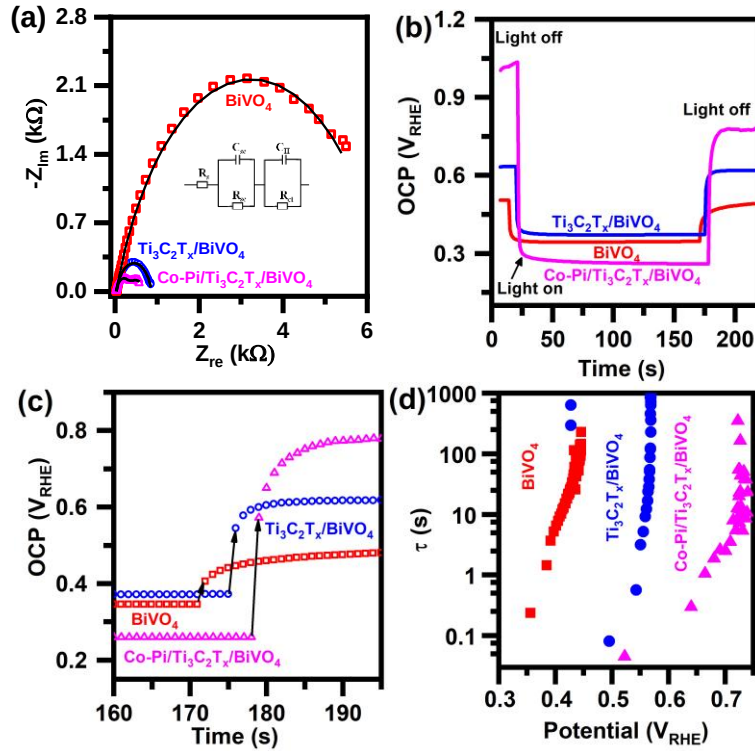


Figure 3.14. (a, b, c, and d) Nyquist, OCP, OCP transient plots, and τ values of pristine BiVO₄, Ti₃C₂T_x/BiVO₄, and Co-Pi/Ti₃C₂T_x/BiVO₄ photoanodes. Condition: part a: potential is 0.8 V_{RHE} and 1.0 M borate buffer pH 9.0.

$$\tau = \frac{k_B T}{e} \left(\frac{dOCP}{dt} \right)^{-1} \quad (3.2)$$

Where τ is the carrier lifetime which depends on potential, k_B is the Boltzmann constant, T is the absolute temperature, e is the charge on an electron, and V_{OC} is the open circuit potential at lifetime (τ). The ΔOCP value of modified photoanodes is greater than pristine BiVO₄, which indicated better charge separation in modified photoanodes than pristine BiVO₄. Figure 3.14(c and d) shows the τ values of all photoanodes, and their values are 0.24 s, 0.08 s, and 0.04 s for pristine BiVO₄, Ti₃C₂T_x/BiVO₄, and Co-Pi/Ti₃C₂T_x/BiVO₄ photoanodes, respectively. The shorter τ value of modified photoanodes indicates that, under illumination, there is a significant enhancement in charge separation and accumulation of charges at the surface of modified photoanodes than pristine BiVO₄. Once the light is switched off, the electrons recombine fast with the accumulated holes at the surface.

The flat-band potentials (E_{fb}) of all electrodes were estimated from the Mott-Schottky (M-S) plots shown in Figure 3.15a. The value of E_{fb} is 0.80 V_{RHE} for all electrodes. It means that there is no significant influence of MXene and Co-Pi deposition on flat-band potential. The donor density values of BiVO₄, Ti₃C₂T_x/BiVO₄, and Co-Pi/Ti₃C₂T_x/BiVO₄ photoanodes are 1.72×10^{19} , 1.40×10^{20} , and 1.64×10^{20} , respectively. Such results can be explained by considering that higher electron density is induced in modified photoanodes after modification with Ti₃C₂T_x MXenes.[159] To intensely understand the effect of Co-Pi/Ti₃C₂T_x on BiVO₄ photoanode on charge transfer and recombination, the transient photocurrent decay occurring immediately upon illumination was evaluated. Figure 3.15b represents the transient photocurrent of all photoanodes at 1.23 V_{RHE} when the light is switched on and off. At light on, an anodic photocurrent spike was observed due to the sudden and rapid evacuation of trapped electrons in the surface states. The anodic spike areas of Ti₃C₂T_x/BiVO₄ and Co-Pi/Ti₃C₂T_x are relatively small relative to that of BiVO₄ indicating that the Co-Pi and Ti₃C₂T_x passivate the surface states. This can be further assured by the absence of cathodic spikes upon the light is turned off. The accumulation of holes in surface defects would cause a large cathodic spike when the light is turned off, and electrons present in the conduction band react with them. There is no cathodic transient observed in Figure 3.15c, suggesting that the accumulation of holes at the surface defects is not the main recombination pathway and Ti₃C₂T_x can effectively transfer the photogenerated holes to the electrolyte solution. The transient decay time ($\ln D$) in the photoanodes was calculated from Equation 3.1. The transient decay time is the time at which the $\ln D = -1$. Based on the transient photocurrent profile measured in Figure 3.15c, the transient decay time of BiVO₄, Ti₃C₂T_x/BiVO₄, and Co-Pi/Ti₃C₂T_x/BiVO₄ photoanodes

are presented in Figure 3.15d. The transient decay times of Co-Pi/Ti₃C₂T_x/BiVO₄ photoanode is 2.80 s which is 2.5 and 11.0 times higher than Ti₃C₂T_x/BiVO₄ (1.10 s) and pristine BiVO₄ (0.26 s), respectively. Based on the above analysis of charge carrier dynamics, it demonstrates that the MXene layer acts as a hole transport layer. It blocks the surface recombination of electron/hole pairs allowing the electrons to stay for a longer time. The Co-Pi further enhances this effect together with its catalysis role in the water oxidation reaction.

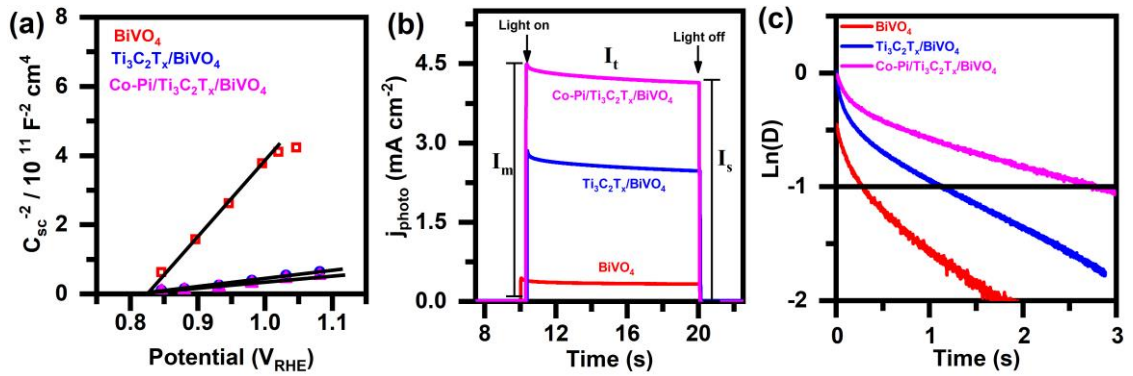


Figure 3.15. (a) Mott-Schottky plots of pristine BiVO₄, Ti₃C₂T_x/BiVO₄, and Co-Pi/Ti₃C₂T_x/BiVO₄ photoanodes measured at 1.0 kHz in dark in 1.0 M borate buffer solution pH 9.0, (b) Transient photo-responses show the chopped current densities (light on/light off) as a function of time, (c) the transient decay time for the same electrodes.

The synergy between Ti₃C₂T_x and BiVO₄ and its influence on the charge transfer kinetics has been further explained through IMPS studies. Figure 3.16(a-c) shows the typical responses of IMPS of the pristine BiVO₄, Ti₃C₂T_x/BiVO₄, and Co-Pi/Ti₃C₂T_x/BiVO₄ photoanodes, respectively. These three Figures contain two semicircles, one is in the 1st quadrant and the other is in the 4th quadrant. The high frequency (HF) semicircle starts from the 4th quadrant, which represents RC attenuation and comprises the total resistance of the cell and the combined capacitance of the space charge layer and Helmholtz layer capacitance. The charge transfer and recombination processes dominate the response in the 1st quadrant (LF semicircle). The rate constants of charge transfer (k_{tr}) and charge

recombination (k_{rec}) at different potentials can be analyzed from the LF semicircles of IMPS results. The LF intercepts are related to surface charge transfer efficiency (η_{ct}) and $\eta_{ct} = k_{tr}/(k_{tr} + k_{rec})$, whereas $\omega_{max} = 2\pi f_{max} = k_{tr} + k_{rec}$. [160] From these equations k_{rec} , k_{tr} , and η_{ct} at various potentials are calculated and are presented in Figure 3.16(d-f) for the pristine BiVO₄, Ti₃C₂T_x/BiVO₄, and Co-Pi/Ti₃C₂T_x/BiVO₄ photoanodes. The k_{rec} value of Ti₃C₂T_x/BiVO₄ is higher than pristine BiVO₄ and Co-Pi/Ti₃C₂T_x/BiVO₄ photoanodes. Considering the fact that k_{tr} and k_{rec} are phenomenological rate constants and they may depend on the hole charge carrier concentration, it can be concluded that the high value of k_{rec} in the presence of MXene is due to the accumulated holes in the Mxene layer. The Co-Pi modification facilitates the electron transfer at the interface and thus the concentration of the accumulated holes is reduced and consequently, the k_{rec} is also decreasing. This finding is consistent with the carrier lifetime extracted from the photovoltage change at the OCP presented in Figure 3.14c. As shown in Figure 3.16e, the k_{tr} values are in the order of Ti₃C₂T_x/BiVO₄ > Co-Pi/Ti₃C₂T_x/BiVO₄ > BiVO₄. The Ti₃C₂T_x/BiVO₄ exhibited the highest k_{tr} values at relatively high bias, despite, it also exhibiting the highest k_{rec} . However, the Ti₃C₂T_x layer has a positive impact as a hole storage layer and facilitates the charge transfer, the high recombination rate is still an issue. It seems that the charge transfer kinetics for Ti₃C₂T_x/BiVO₄ photoanode is superior, but the charge recombination limits the overall PEC activity. The overall performance of the photoelectrode is governed by the charge transfer and recombination and thus the charge transfer efficiency is calculated for all electrodes and presented in Figure 3.16f. The Co-Pi/Ti₃C₂T_x/BiVO₄ photoanode showed the highest efficiency in agreement with the photocurrent responses presented in 3.13b. Based on the analysis of the

photoelectrochemical results it seems that the $\text{Ti}_3\text{C}_2\text{T}_x$ layer acts as a hole storage layer. Increasing the concentration of the photogenerated holes at the surface will increase the charge transfer, but also will increase the rate of the recombination with the conduction band electrons. Despite that, it has a positive impact on the overall performance. The enhancement in k_{tr} and charge transfer efficiency after the deposition of $\text{Ti}_3\text{C}_2\text{T}_x\text{MXene}$ on the BiVO_4 is further explained due to the difference in the work function of $\text{Ti}_3\text{C}_2\text{T}_x\text{MXene}$ and BiVO_4 . The work function of $\text{Ti}_3\text{C}_2\text{T}_x\text{MXene}$ is 5.0 eV [161], which is higher than pristine BiVO_4 (4.15 eV). When the BiVO_4 and $\text{Ti}_3\text{C}_2\text{T}_x\text{MXene}$ layers are connected, a strong built-in electric field is produced at the $\text{Ti}_3\text{C}_2\text{T}_x/\text{BiVO}_4$ Schottky junction and the space charge layer width is enhanced (see Figure 3.17).[79] So, the photo-generated holes are easily transferred from the valence band of BiVO_4 to $\text{Ti}_3\text{C}_2\text{T}_x\text{MXene}$, and these transferred holes in the $\text{Ti}_3\text{C}_2\text{T}_x\text{MXene}$ layer are immediately used for water oxidation. At the same time, electrons in the conduction band of BiVO_4 are not able to cross this Schottky barrier.

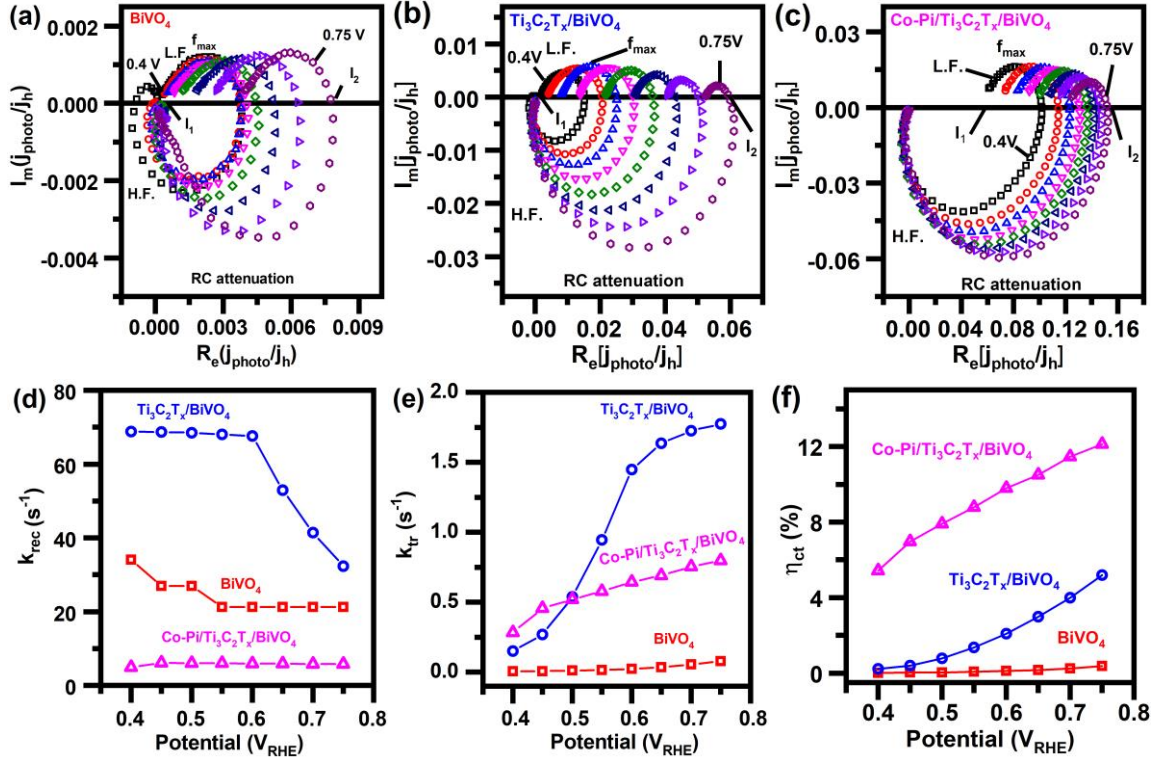


Figure 3.16. IMPS responses were measured for (a) Pristine BiVO₄, (b) Ti₃C₂T_x/BiVO₄, and (c) Co-Pi/Ti₃C₂T_x/BiVO₄ photoanodes at various applied potentials in 1.0 M borate buffer (pH 9.0) and potential dependence of the rate constants of (d) charge recombination (k_{rec}), (e) charge transference (k_{tr}), and (f) Charge transfer efficiencies (η_{ct}) of BiVO₄, Ti₃C₂T_x/BiVO₄, and Co-Pi/Ti₃C₂T_x/BiVO₄ photoanodes.

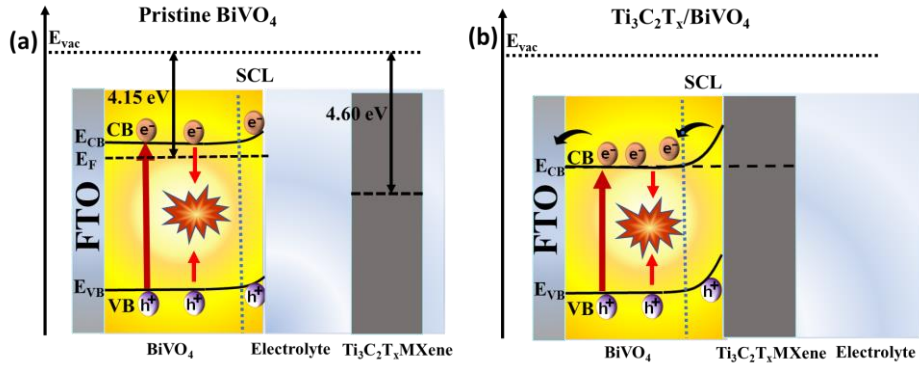


Figure 3.17. Energetic schemes of before (a) pristine BiVO₄ and after Schottky junction formation (b) Ti₃C₂T_x/BiVO₄ photoanodes.

3.3. BiVO₄ Photoanode with NiV₂O₆ Back Contact Interfacial Layer

The XRD patterns of Ni(OH)₂, pristine BiVO₄, NiV₂O₆/BiVO₄, and Co-Pi/NiV₂O₆/BiVO₄ films are represented in Figure 3.18a. The diffraction peaks indicated by the star (*) symbol in the XRD spectra can be well indexed for monoclinic BiVO₄ (JCPDS no. 14-0688).[50] The other peaks, referred to by the (o) symbol, are for the F-SnO₂ layer of the conductive glass substrate (JCPDS card no. 041-1445).[26] From Figure 3.18a, there are no diffraction peaks observed for the Ni(OH)₂, NiV₂O₆, and Co-Pi layers, likely due to their low concentrations. Raman spectroscopy is more sensitive and thus we used it to confirm the formation of NiV₂O₆. The Raman scattering spectra of pristine BiVO₄ and NiV₂O₆/BiVO₄ films in Figure 3.18b and Ni(OH)₂ and pristine NiV₂O₆, are presented in Figure 3.18c. The Raman spectrum of pristine BiVO₄ contains five vibration peaks at 212, 323, 366, 707, and 823 cm⁻¹ corresponding to stretching and bending vibrations of the V-O bond in the BiVO₄. The intense band at 823 cm⁻¹ is attributed to the shorter symmetric V-O stretching mode (A_{1g}) and the weak band at 707 cm⁻¹ is assigned to the long (A_{1g}) asymmetric V-O stretching mode. The asymmetric and symmetric bending vibrations of the VO₄ tetrahedron are detected at 323 and 366 cm⁻¹, respectively.[162] The NiV₂O₆ has Raman peaks located at 280 cm⁻¹ due to Ni-O vibration and at 935, 690, and 585 cm⁻¹ due to the V-O shorter symmetric stretching (A_{1g}), and asymmetric long stretching (A_{2g}) and short asymmetric (A_{3g}) vibrations, respectively. The two bands that appeared below 200 cm⁻¹ are ascribed to the lattice vibrations.[163, 164] For comparison the the Raman spectrum of Ni(OH)₂ has been also added to Figure 3.18b. Ni(OH)₂ has Raman peaks at 320 and 448 cm⁻¹ which are identified to be translational A_{1g}(T) and E_g(T) phonons while the Raman peak at 861 cm⁻¹ is assigned to the rotational E_g(R) mode. For the NiV₂O₆/BiVO₄ film, ten Raman

peaks have been detected. Five of them (i.e. 212, 327, 369, 708, and 827 cm^{-1}) can be readily indexed to the BiVO_4 . The other five peaks are located at 124, 144, 280, 589, and 941 cm^{-1} and can be assigned to the stretching and bending vibration modes of NiV_2O_6 . The little shift observed in $\text{NiV}_2\text{O}_6/\text{BiVO}_4$ Raman bands relative to the pristine NiV_2O_6 and BiVO_4 indicates the electronic interaction between them. The appearance of both BiVO_4 and NiV_2O_6 Raman peaks confirms the coexistence of $\text{NiV}_2\text{O}_6/\text{BiVO}_4$.

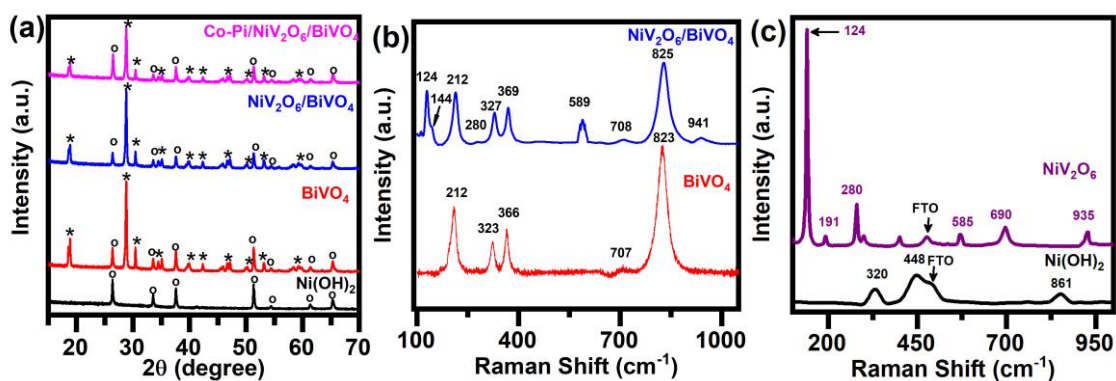


Figure 3.18. (a) XRD diffraction patterns of Ni(OH)_2 , pristine BiVO_4 , $\text{NiV}_2\text{O}_6/\text{BiVO}_4$, and $\text{Co-Pi/NiV}_2\text{O}_6/\text{BiVO}_4$ photoanodes. Star (*) and hollow circle (o) symbols indicate the Bragg diffraction peaks of BiVO_4 and FTO, respectively. (b) Raman spectra of pristine BiVO_4 and $\text{NiV}_2\text{O}_6/\text{BiVO}_4$ heterostructure photoanodes.

Figure 3.19 shows the low magnification FE-SEM images of the synthesized Ni(OH)_2 , BiVO_4 , $\text{NiV}_2\text{O}_6/\text{BiVO}_4$, and $\text{Co-Pi/NiV}_2\text{O}_6/\text{BiVO}_4$ films grown on the FTO substrate. Low magnification images are presented here to represent to a greater extent the overall quality of the film rather than focusing on a small area. Figure 3.19a represents the vertically standing nanosheets of Ni(OH)_2 on the FTO substrate, which are continuously interconnected with one another, and the film has no cracks and is free of pinholes. Controversially, the SEM image of pristine BiVO_4 (Figure 3.19b), fabricated in the absence of Ni(OH)_2 film, is discontinuous and exhibits pinholes between the secondary particles that consist of small primary particles of 95 nm. The SEM image of $\text{NiV}_2\text{O}_6/\text{BiVO}_4$ shown in Figure 3.19c indicated that the use of Ni(OH)_2 layer leads to the formation of a

continuous and pinholes-free film. Figure 3.19d shows the FE-SEM image of the Co-Pi/NiV₂O₆/BiVO₄ film. No significant change in the morphology has been observed after the deposition of Co-Pi on the top surface of the NiV₂O₆/BiVO₄ film. The thickness of pristine BiVO₄ and NiV₂O₆/BiVO₄ films were estimated from the cross-sectional FE-SEM image presented in Figure 3.19(e & f), respectively. Figure 3.19e shows the typical worm-like morphology of pristine BiVO₄ and the film is approximately 840 nm. The thickness of NiV₂O₆/BiVO₄ film is approximately 1250 nm. The film is thicker than that of pristine BiVO₄ and has a porous structure. The EDX analysis of the bottom and upper parts of the NiV₂O₆/BiVO₄ film (Figure 3.19e) showed that the bottom part which is near the FTO substrate contains a higher quantity of Ni, while the upper layer is rich in Bi suggesting the formation NiV₂O₆ BCI layer between BiVO₄ and FTO substrate. The transmission electron microscopy (TEM) measurements were performed to further investigate the formation of NiV₂O₆/BiVO₄ heterostructure. The low-magnification TEM image shown in Figure 3.19g indicates that the NiV₂O₆/BiVO₄ film is composed of interconnected nanoparticles. Meanwhile, the high-resolution image (Figure 3.19h) indicated the formation of NiV₂O₆/BiVO₄ heterostructure. The NiV₂O₆ lattice fringes were observed with an interplanar distance of 0.24 nm corresponding to the (012) facet.[165] The lattice spacing of 0.31 nm could be indexed to the (130) reflections of monoclinic BiVO₄.[166]

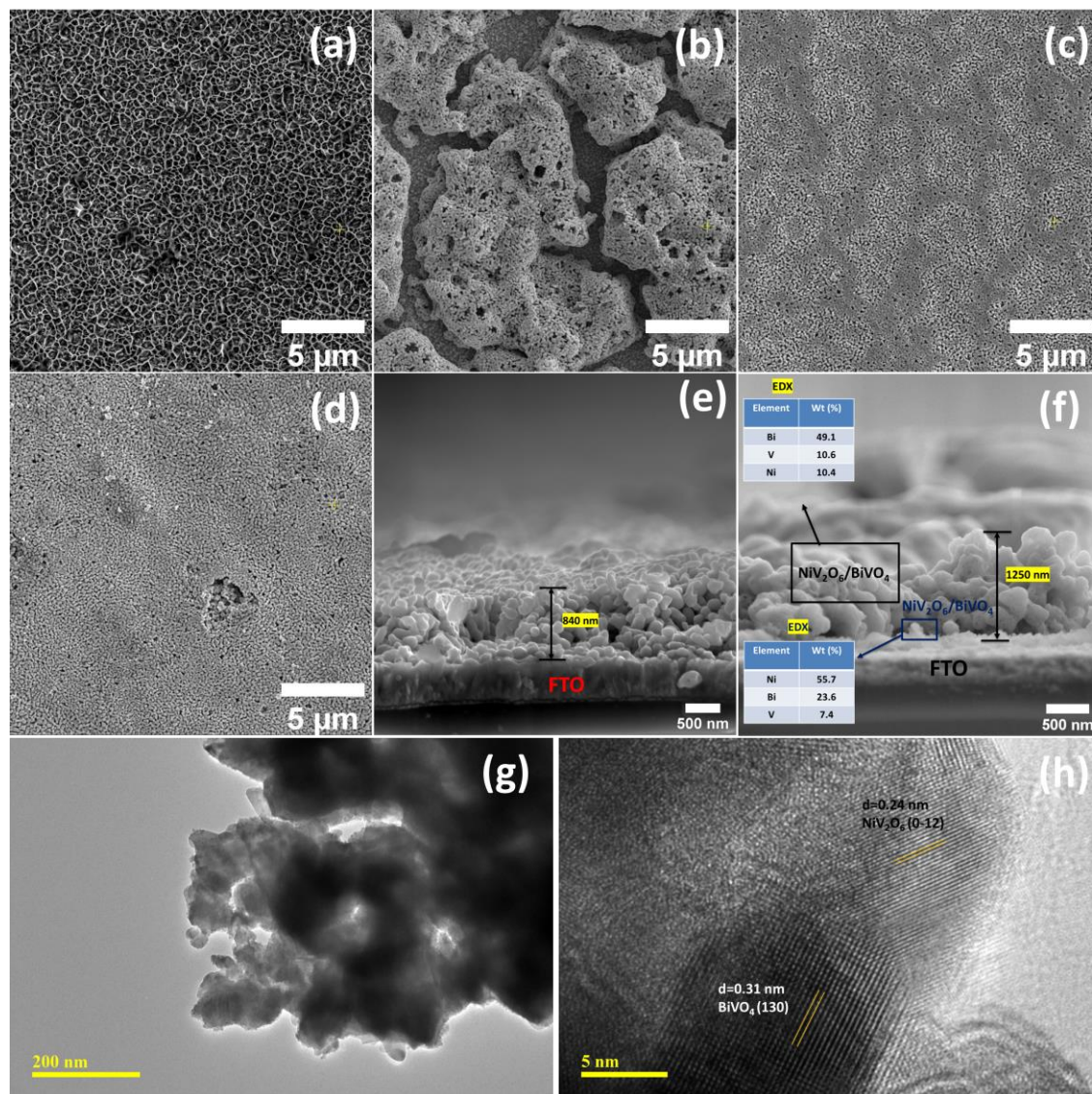


Figure 3.19. Top view FE-SEM images of (a) Ni(OH)₂, (b) pristine BiVO₄, (c) NiV₂O₆/BiVO₄, and (d) Co-Pi/NiV₂O₆/BiVO₄ films; and (e & f) cross-sectional FE-SEM images of pristine BiVO₄ and NiV₂O₆/BiVO₄ films, respectively; (g & h) TEM images of NiV₂O₆/BiVO₄ heterostructure at low and high magnification.

Figure 3.20a shows the absorption spectra of all films, and all of them exhibit absorbance edges around 500 nm, suggesting no modification for the bandgap. This further suggested that the enhancement in the photocurrent of the Co-Pi/NiV₂O₆/BiVO₄ photoanode is mainly due to the enhancement in the charge transfer and separation efficiencies. The optical bandgap energies of pristine BiVO₄, NiV₂O₆/BiVO₄, and Co-Pi/NiV₂O₆/BiVO₄ were calculated from absorption spectra using the Tauc's plot presented in Figure 3.20b

assuming indirect bandgap transition.[167] A bandgap of 2.44 eV was observed for all films.

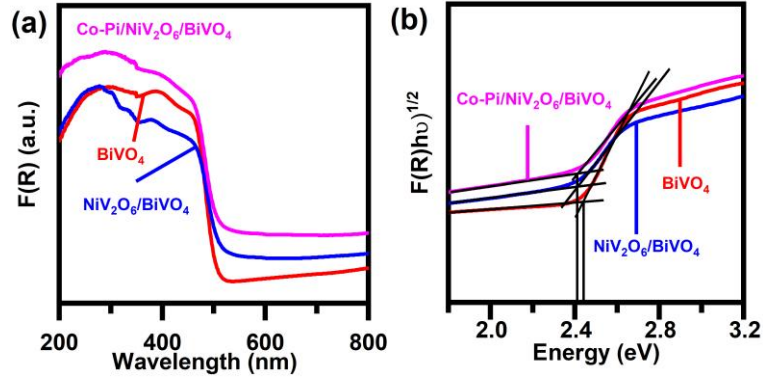


Figure 3.20. (a) UV-vis absorption spectra and inset (b) Tauc's plots of pristine BiVO₄, NiV₂O₆/BiVO₄, and Co-Pi/BiVO₄/NiV₂O₆ photoelectrodes.

The surface chemical composition and oxidation states of elements of pristine BiVO₄ and NiV₂O₆/BiVO₄ films were determined by XPS and presented in Figure 3.21. Figure 3.21a shows the XPS spectra of bismuth 4f core levels. The doublet peaks appear at 164.6 eV and 159.2 eV representing the binding energies of Bi 4f_{5/2} and Bi 4f_{7/2} respectively, indicating that Bi exists in +3 oxidation state.[168] The XPS spectra of Ni 2p core levels in NiV₂O₆/BiVO₄ film before and after etching are presented in Figure 3.21b. No Ni peaks were observed before etching evincing that the top layer is mainly BiVO₄. After etching, the characteristic peaks of Ni²⁺ located at 873.3 eV and 856.0 eV have been observed. The peaks that appeared at 879.6 eV and 861.8 eV belong to the satellite peaks.[169] From Figure 3.21c, the V 2p binding energy peaks at 524.6 and 516.7 eV confirm that the V presents in a +5 oxidation state.[170] A broad XPS spectra are observed for the O 1s in pristine BiVO₄ and NiV₂O₆/BiVO₄ (Figure 3.21d) indicating that there are different chemical environments. The XPS spectrum of O 1s in pristine BiVO₄ can be deconvoluted into three peaks, the peaks at 529.9 and 531.5 eV are assigned to the lattice oxygen and

oxygen defects, respectively, while the peak observed at 532.7 eV is due to hydroxyl groups and water molecules adsorbed at the surface. The O 1s XPS spectrum of the etched $\text{NiV}_2\text{O}_6/\text{BiVO}_4$ sample can be deconvoluted into two peaks located at 530.2 and 532.2 eV which are assigned to lattice oxygen and oxygen defects. The peak of the adsorbed water molecules is missing due to the etching.[171]

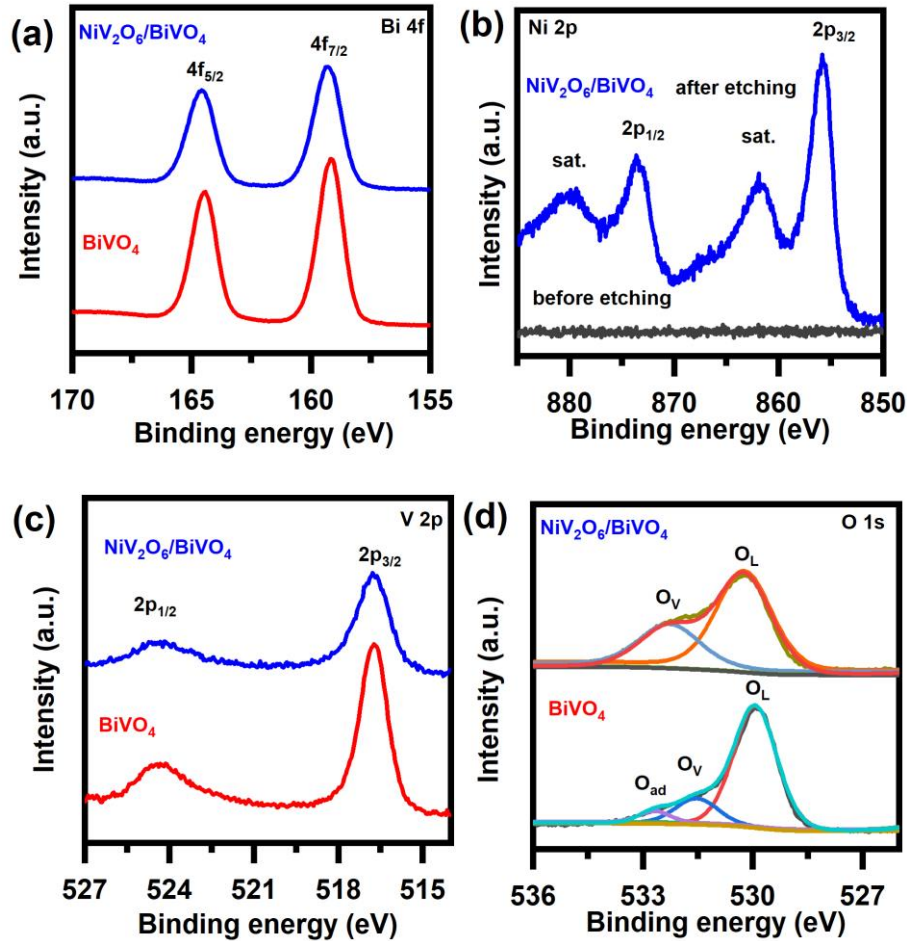


Figure 3.21. XPS spectra of (a) Bi 4f, (b) Ni 2p, (c) V 2p, and (d) O 1s of pristine BiVO_4 and $\text{NiV}_2\text{O}_6/\text{BiVO}_4$ films. The influence of the drop-casting solution's composition and $\text{Ni}(\text{OH})_2$ film's deposition time on the PEC performance of $\text{NiV}_2\text{O}_6/\text{BiVO}_4$ photoanode was investigated. First, the deposition time for $\text{Ni}(\text{OH})_2$ film on the FTO substrate was fixed to 30 min. Then, drop-casting solutions containing different Bi atomic ratios (i.e. 0.0 - 100% Bi at.% calculated as $[\text{Bi}]/([\text{Bi}]+[\text{V}])$) were used to fabricate the photoelectrodes. Figure 3.23a shows the

generated photocurrent densities at 1.23 V_{RHE} for the resulted photoanodes as a function of the Bi at.%. The photocurrent was measured in the absence and presence of Na₂SO₃ electron donors. In both cases, the maximum photocurrent was achieved at 43 at.% of Bi, which is 0.65 ± 0.08 mA/cm² and 5.4 ± 0.22 mA/cm² in the absence and presence of Na₂SO₃ (0.5 M), respectively. For simplicity, we keep using the abbreviation NiV₂O₆/BiVO₄ for the photoanode prepared using the drop-casting solution with this composition (optimized [Bi]/([Bi]+[V]) ratio). It is worth mentioning that the illumination in this study was done from the back side and thus the thickness of the BCI layer is crucial. If the thickness of the BCI layer is high, it could shield the light and induce back-surface recombination. Therefore, we have optimized the thickness of the BCI layer by varying the deposition time of the Ni(OH)₂ sacrificial film (Figure 3.22a). It was found that 30 min deposition time is the optimum and the best annealing temperature for getting NiV₂O₆/BiVO₄ with high PEC performance is 450 °C (Figure 3.22b). Figure 3.23b shows the linear sweep voltammograms (LSVs) of BiVO₄, NiV₂O₆/BiVO₄, and Co-Pi/NiV₂O₆/BiVO₄ photoanodes in the absence and presence of Na₂SO₃. The BiVO₄/NiV₂O₆ photoanode showed a significant increase in photocurrent compared to BiVO₄ in the presence of Na₂SO₃. In the absence of Na₂SO₃ ions, both electrodes exhibited comparable performance. These results show that more holes can diffuse and reach the surface of NiV₂O₆/BiVO₄ compared to BiVO₄ but the former still suffers from a high surface recombination rate. It is known that Co-Pi cocatalyst can passivate the surface defects and accelerate the water oxidation kinetics.[52] Indeed, the modification of NiV₂O₆/BiVO₄ with Co-Pi (Co-Pi/NiV₂O₆/BiVO₄) has enhanced dramatically the PEC performance in the absence of Na₂SO₃ electron donors (Figure 3.23c). The back-side illumination gives higher PEC activity,

particularly, for the Co-Pi/NiV₂O₆/BiVO₄, and implies that the photogenerated holes generated at the back side can diffuse and reach the electrode/electrolyte interface more efficiently in the presence of the BCI layer. This assumption has been supported later by determining the recombination rate constants and hole diffusion length. Under standard illumination, Co-Pi/NiV₂O₆/BiVO₄ could deliver 4.8 mA/cm² at 1.23 V_{RHE} which is approximately 2 times higher than Co-Pi/BiVO₄ (2.36 mA/cm²), 8 times higher than NiV₂O₆/BiVO₄ (0.65 mA/cm²) and 12 times higher than pristine BiVO₄ (0.42 mA/cm²). The incident photon-to-current conversion efficiency (IPCE) of pristine BiVO₄, NiV₂O₆/BiVO₄, and Co-Pi/NiV₂O₆/BiVO₄ photoanodes at 1.23 V_{RHE} measured in the absence of electron donors are presented in Figure 3.23d. The Co-Pi/NiV₂O₆/BiVO₄ photoanode shows a maximum IPCE value of 61% at 420 nm. It also showed a high applied bias photon-to-current efficiency (ABPE) value of 0.83 % (Figure 3.23e) at a Faradaic efficiency of 85 %. The ABPE was evaluated using a two-electrode configuration to account for the reaction at both electrodes.[172] The charge separation efficiency (η_{sep}) was also calculated[173] and the results are plotted in Figure 3.22 (e and f). The details of the calculation are given in the supporting information. It was found that the η_{sep} of NiV₂O₆/BiVO₄ and pristine BiVO₄ are low throughout the applied potential window envincing the high surface recombination and low charge transfer efficiency at both photoanodes. However, after Co-Pi deposition, the Co-Pi/NiV₂O₆/BiVO₄ photoanode showed approximately 7.5 and 10-fold enhancement in η_{sep} at 1.23 V_{RHE} than NiV₂O₆/BiVO₄ and BiVO₄ photoanodes, which is consistent with the LSV results and supported later by IMPS analysis. Figure 3.22f shows the Nyquist plots at various potentials (0.5-0.8 V_{RHE}). It can be concluded from the reduced semicircle size that the

charge transfer for water is greatly reduced after the modification with Co-Pi in agreement with previous reports.[174] The long-term stability test, presented in Figure 3.23f, indicated that the Co-Pi/NiV₂O₆/BiVO₄ photoanode exhibits excellent stability for over 25 hours at an applied potential of 0.6 V_{RHE}. Considering our facile recipe, the developed Co-Pi/NiV₂O₆/BiVO₄ photoanode exhibits considerable PEC activity and stability relative to those of the most active BiVO₄-based photoanodes (Table 1.2). The remarkable PEC performance is mainly due to the better charge separation induced by the BCI layer at the back interface and the facile water oxidation by the Co-Pi OEC at the front interface. To assess the Faradaic efficiency of water oxidation on the Co-Pi/NiV₂O₆/BiVO₄ photoanode, the rate of PEC O₂ and H₂ evolution was measured and presented in Figure 3.23g. A sealed single-chamber PEC cell connected with gas chromatography was used to quantify the generated O₂ and H₂ gases at the photoanode and counter electrode, respectively. An H₂/O₂ ratio of almost 2/1 was achieved and the Faradaic efficiency of the oxygen evolution reaction was 85 %. The other 15 % might be due to the formation of liquid phase species (e.g. H₂O₂) and dissolved oxygen.[175]

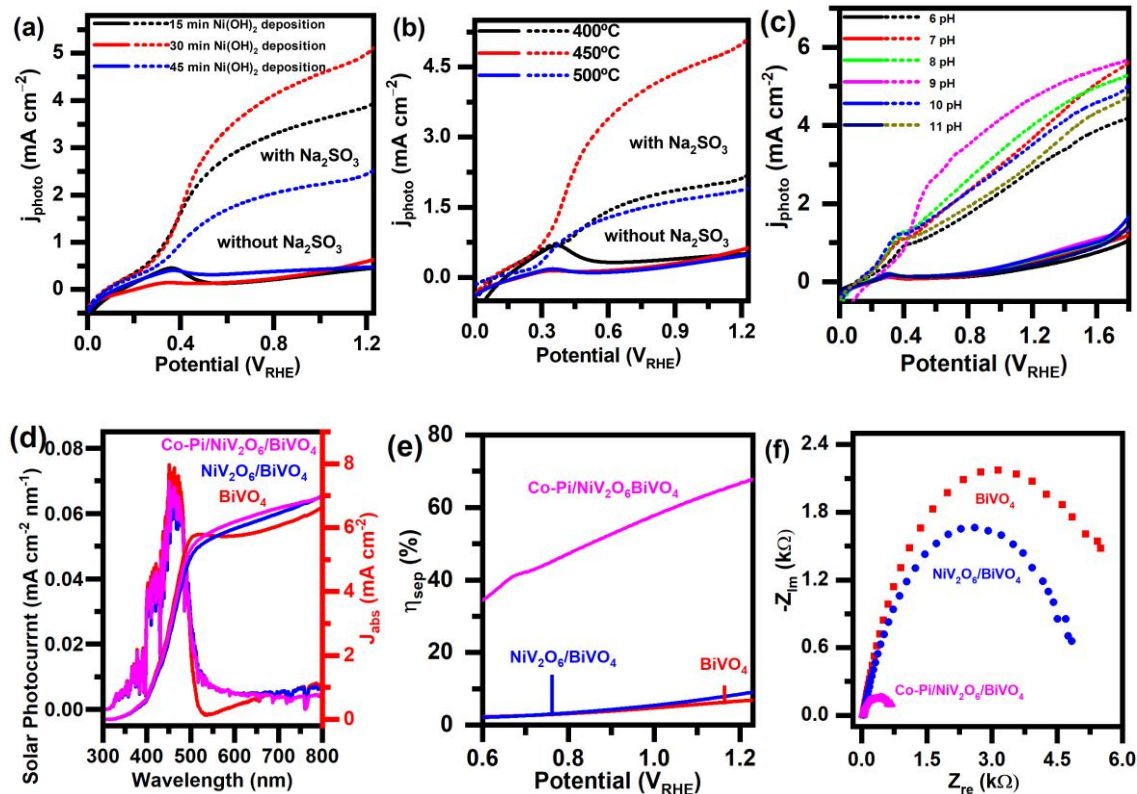


Figure 3.22. (a & b) Influence of the chemical deposition time of Ni(OH)_2 layer and annealing temperature on the PEC performance of $\text{NiV}_2\text{O}_6/\text{BiVO}_4$ photoanodes respectively, (c) I - V curves for $\text{NiV}_2\text{O}_6/\text{BiVO}_4$ and $\text{Co-Pi/NiV}_2\text{O}_6/\text{BiVO}_4$ photoanodes in different pH of borate buffers, and (d & e) J_{abs} and calculated Charge separation efficiencies of pristine BiVO_4 , $\text{NiV}_2\text{O}_6/\text{BiVO}_4$, and $\text{Co-Pi/NiV}_2\text{O}_6/\text{BiVO}_4$ photoanodes, and (f) Nyquist plots of BiVO_4 , $\text{NiV}_2\text{O}_6/\text{BiVO}_4$, and $\text{Co-Pi/NiV}_2\text{O}_6/\text{BiVO}_4$ photoanodes at 0.8 V_{RHE} .

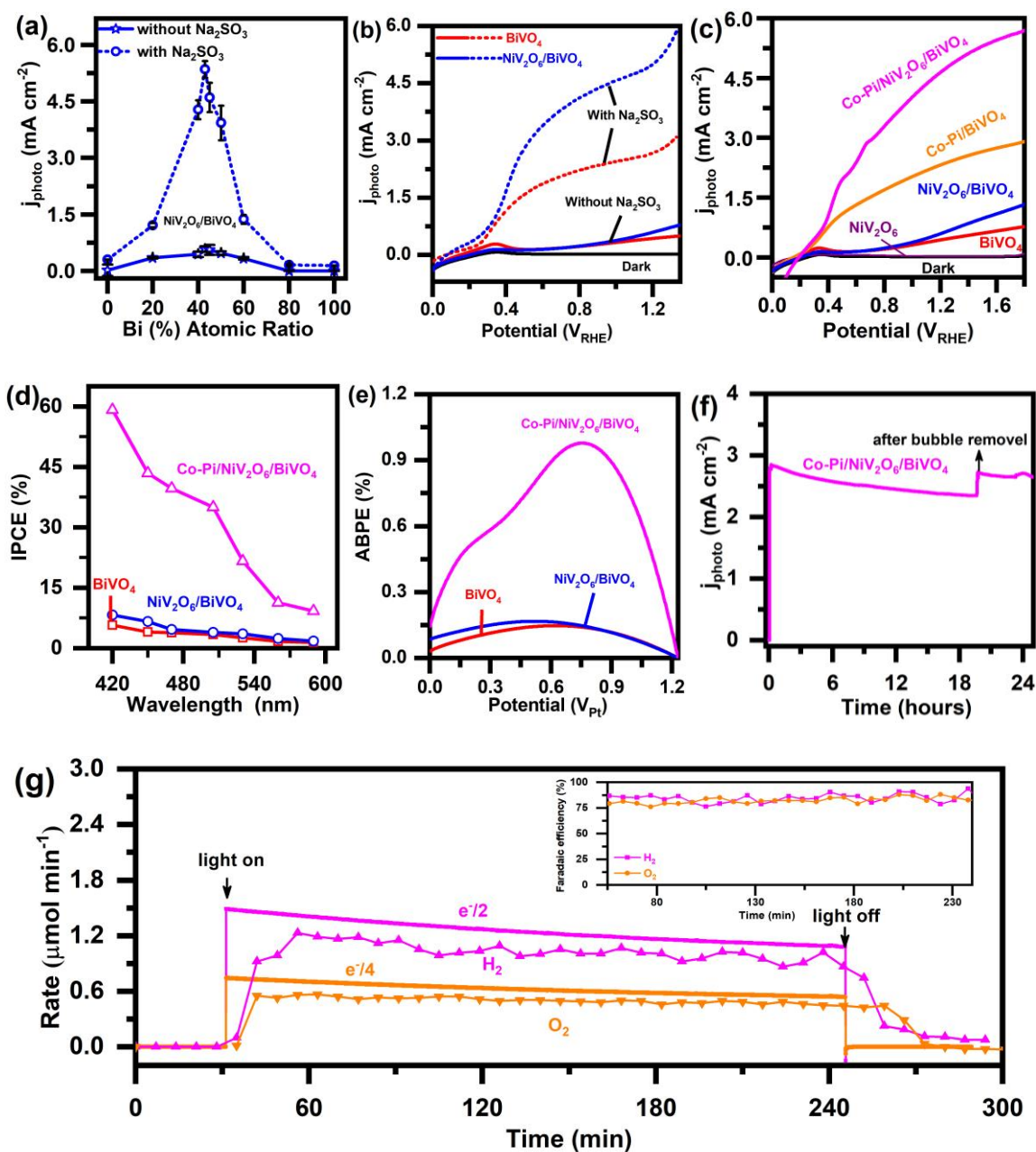


Figure 3.23. (a) Photocurrent measured at 1.23 V_{RHE} versus the atomic ratio of Bi in the drop-casting solution; (b, c, and d) LSVs and IPCE % of BiVO_4 , $\text{NiV}_2\text{O}_6/\text{BiVO}_4$, and $\text{Co-Pi/NiV}_2\text{O}_6/\text{BiVO}_4$ photoanodes; (e) ABPE of BiVO_4 , $\text{NiV}_2\text{O}_6/\text{BiVO}_4$, and $\text{Co-Pi/NiV}_2\text{O}_6/\text{BiVO}_4$ photoanodes; (f) Chronoamperometric stability test for $\text{Co-Pi/NiV}_2\text{O}_6/\text{BiVO}_4$ photoanode measured at 0.6 V_{RHE}, and (g) Rate of PEC H_2 and O_2 evolution from 1.0 M borate buffer (pH=9.0) at 1.23 V_{RHE} and inset figure shows the H_2 and O_2 Faraday efficiencies. Electrolyte: 1.0 M borate buffer solution (pH 9.0) with or without Na_2SO_3 as indicated in the figure.

Up to here, it has been found that the creation of a NiV_2O_6 BCI layer between the BiVO_4 layer and FTO substrate enhances the availability of holes at the surface. To elucidate this finding more, we have measured the flat band potential (E_{FB}), donor density (N_{D}), and hole

diffusion length for pristine and NiV₂O₆/BiVO₄ photoanodes. The Mott–Schottky (M–S) plots for all electrodes and presented in Figure 3.24a. All electrodes showed positive slopes, suggesting that all exhibit the characteristics of n-type semiconductors. The E_{FB} and N_D values were derived from equations 2.4 and 3.3, respectively [176]

$$N_d = \frac{2}{\varepsilon \varepsilon_0 e_0} \left[\frac{d\left(\frac{1}{C^2}\right)}{dE} \right]^{-1} \quad (3.3)$$

where C is the capacitance, A is the area in cm², ε is the dielectric constant, which is 68 for BiVO₄, ε_0 is the permittivity of free space (8.85×10⁻¹² Fm⁻¹), e is the charge on an electron (1.62×10⁻¹⁹ C), N_D is the charge carrier density (cm⁻³), and E_{app} is the applied potential referenced to the RHE, k_B is the Boltzmann constant, and T is the temperature in K. From the intercept of Figure 3.24a, the E_{FB} values of pristine BiVO₄, NiV₂O₆/BiVO₄, and Co-Pi/NiV₂O₆/BiVO₄ electrodes were calculated as 0.79, 0.73, and 0.73 V_{RHE}, respectively. The E_{FB} of BiVO₄ and NiV₂O₆/BiVO₄ photoanodes extracted from the onset of the J²_{photo}-E curve (see Figure 3.24b) agreed to a great extent with the obtained values from the M–S plots evincing the consistency of the measured values. From the slope of Figure 3.24a and using Equation 3.3, the doping densities (N_D) of pristine BiVO₄, BiVO₄/NiV₂O₆, and Co-Pi/BiVO₄/NiV₂O₆ photoanodes are 1.7×10¹⁹, 2.8×10¹⁹, and 1.9×10²⁰ cm⁻³, respectively. Assuming an ideal semiconductor behavior, the space charge layer (W_{SC}) could be calculated from the following equation 3.4.

$$W_{SC} = W_0 \sqrt{V_{app} - V_{fb}} = \sqrt{\frac{2\varepsilon \varepsilon_0}{e N_D}} \sqrt{V_{app} - V_{fb}} \quad (3.4)$$

It is worth mentioning here that the NiV₂O₆ BCI layer is much thinner than the top BiVO₄ layer (Figure 3.19f), thus it is reasonable to employ M-S analysis for both electrodes using the BiVO₄ dielectric constant. Assuming the recombination in the space charge layer is

neglectable, the maximum distance the holes will travel to reach the surface can be given by:[177]

$$D = W_{SC} + L_{D,eff} = \sqrt{\frac{2\epsilon\epsilon_0}{eN_D}} \sqrt{V_{app} - V_{fb}} + L_{D,eff} \quad (3.5)$$

Where $L_{D,eff}$ is the hole diffusion length, which is independent of applied potential. The condition of low surface recombination can be satisfied to a great extent in the presence of Na_2SO_3 . So, it is reasonable considering that all holes reacting at the surface of photoanodes and reacting with Na_2SO_3 are generated between the surface and the distance D inside the semiconductor. The absence of an anodic spike peak in the transient photocurrent curves presented in Figure 2.24(c & d) and measured in the presence of Na_2SO_3 confirms the validity of this assumption. So, it is reasonable to assume that the current measured is due to the number of positive charges (holes) reaching the surface of the photoanode. Based on the Lambertian absorption and assuming negligible loss in reflection (with Transmittance = 1- Absorption), the distance D can be calculated from equation 3.6:[177]

$$D = -\alpha^{-1} \log(1 - A) = -\alpha^{-1} \log\left(1 - \frac{\Delta j_{ss}}{j_{pulse\ intensity}}\right) \quad (3.6)$$

Where A is the absorption, and α is the absorption coefficient, and its value for BiVO_4 at 430 nm is $4.0 \times 10^{-3} \text{ nm}^{-1}$. [95] Δj_{ss} and $j_{light\ intensity}$ is the photocurrent density and hole current density (corresponding to the light intensity of 430 nm LED), respectively. The ratio between Δj_{ss} and the hole current density is equal to the Lambertian absorption. According to equation 3.6, the graph between the calculated D (from equation 3.6) at different applied potentials versus $(E_{app} - E_{FB})^{1/2}$ should yield a straight line with a y-intercept equal to the hole diffusion length. Indeed, as shown in Figure 3.24c, straight lines with positive y-axis

intercepts have been observed for BiVO₄ and NiV₂O₆/BiVO₄. The calculated hole diffusion length of BiVO₄ was found to be 44 nm which is consistent with the literature value[41] and for NiV₂O₆/BiVO₄ it has been extended to 95 nm. This finding indicates that the NiV₂O₆ BCI layer increases the hole diffusion length by a factor of 2-fold. This is an important reason for the enhanced PEC observed in this study.

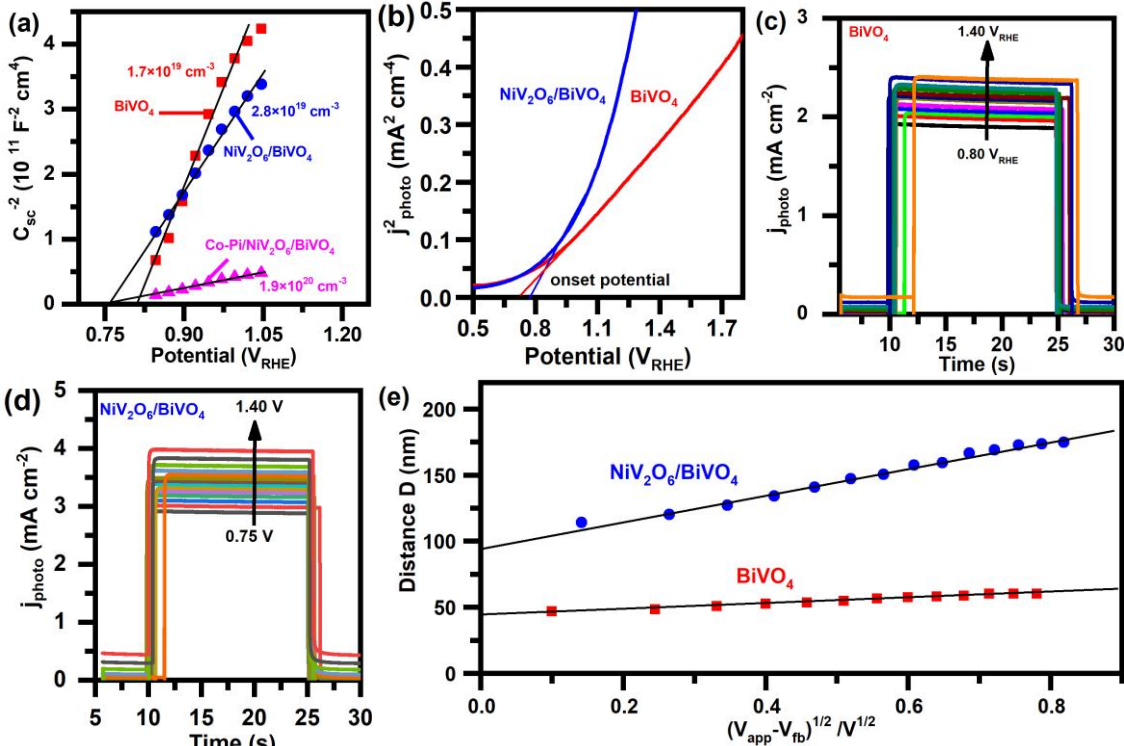


Figure 3.24. (a) Mott-Schottky plots of BiVO₄, NiV₂O₆/BiVO₄, and Co-Pi/NiV₂O₆/BiVO₄ photoanodes; (b) j^2_{photo} -V curve for BiVO₄ and NiV₂O₆/BiVO₄ photoanodes; TPC of (c) pristine BiVO₄, (d) NiV₂O₆/BiVO₄ heterostructure photoanodes in Na₂SO₃, and (e) Plot of D (in nm) versus the square root of the potential drop within the space charge layer for BiVO₄ and NiV₂O₆/BiVO₄.

The generated photovoltage (V_{ph}) was also measured to investigate further the influence of NiV₂O₆/BiVO₄ formation on the PEC performance. In the dark, the OCP_{dark} represents the equilibrium potential with the electrolyte's redox species. Under illumination, the photogenerated holes are captured by the hydroxyl ions present in the electrolyte, while the separated electrons are accumulated at the electrode. The accumulation of electrons shifts the Fermi level toward negative potential, hence the OCP_{light} is cathodically shifted. Once the accumulation of electrons is maximum and reaches a steady state (i.e. electron

separation competes with charge recombination), the V_{ph} is measured as the difference between OCP_{light} and OCP_{dark} from Figure 3.25a. Slight improvement has been observed in the V_{ph} of the $NiV_2O_6/BiVO_4$ (0.21 V) compared to $BiVO_4$ (0.15 V). This agrees well with the little improvement in the photocurrent and confirms that though the creation of the NiV_2O_6 BCI layer increases the hole diffusion length, the high surface recombination limits the PEC performance. The loading of Co-Pi as a passivation material is crucial and significantly enhanced the photovoltage to 0.37 V. When light is turned off accumulated electrons undergo recombination with holes[178] and the potential dependent lifetime (τ) of the accumulated electrons can be calculated by using the model presented by Bisquert and co-workers using equation 3.2:[158] Figure 3.25b shows the decay profiles for the measured V_{OCP} after switching off the light. The τ values for $BiVO_4$, $NiV_2O_6/BiVO_4$, and Co-Pi/ $NiV_2O_6/BiVO_4$ photoanodes have been calculated using Eq. 6 and presented in Figure 3.25c. A comparable electron lifetime was observed for $BiVO_4$ and $NiV_2O_6/BiVO_4$ indicating that the formation of the NiV_2O_6 BCI layer does not significantly alter the kinetics of electron reaction with the surface states and/or surface-trapped holes at the electrode/electrolyte interface.[179] A shorter electron lifetime was observed after the loading of Co-Pi evincing that the Co-Pi passivates the surface states effectively and thus the accumulated electrons can fast react with the surface accumulated holes once the light is off. To further confirm this finding, the rate constants for surface recombination (k_{rec}) and transfer rate (k_{tr}) were calculated using the IMPS technique.[180] Figure 3.26(a-c) showed the IMPS responses of pristine $BiVO_4$, $NiV_2O_6/BiVO_4$, and Co-Pi/ $NiV_2O_6/BiVO_4$ photoanodes. The IMPS spectra contain two semicircles, the lower semicircle corresponds to resistance-capacitance attenuation (RC attenuation) and the upper semicircle

corresponds to the competition between charge recombination and charge transfer.[181] The upper semicircle can be used to determine k_{rec} and k_{tr} using the equation ($k_{rec}+k_{tr} = 2\pi f_{max} = \omega_{max}$) and the normalized low frequency (L.F.) intercept ($I_1 = k_{tr}/(k_{rec}+k_{tr})$).[182, 183] The latter corresponds to charge transfer efficiency (η_{ct}).

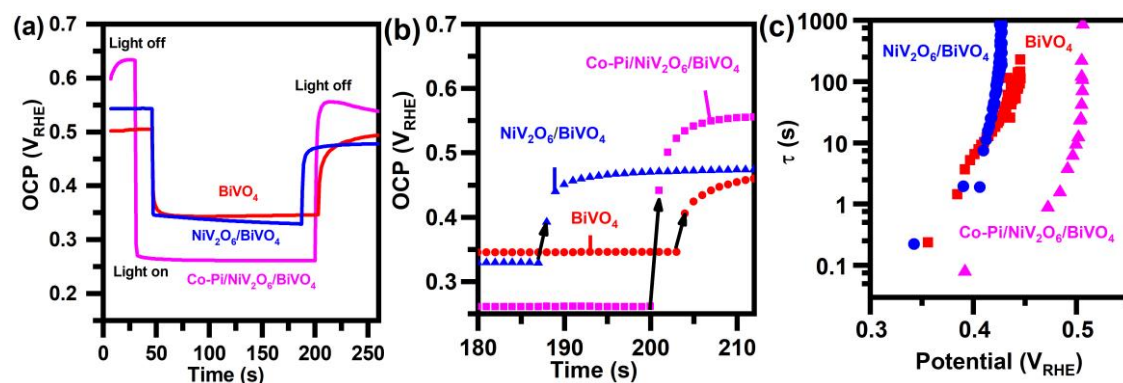


Figure 3.25. (a) Open circuit potential (OCP) and (c) carrier lifetime derived from OCP decay curves presented in part (b) for BiVO₄, NiV₂O₆/BiVO₄, and Co-Pi/NiV₂O₆/BiVO₄ photoanodes. Indeed, it can be seen from the k_{rec} values presented in Figure 3.25d that the NiV₂O₆/BiVO₄ photoanode exhibits the highest recombination rate however it has a higher hole diffusion length than that of BiVO₄. The long hole diffusion length will allow more holes to reach the surface, but it seems that not all of them can be involved in the water oxidation and thus the electron/hole surface recombination will be increased as well.[184] The passivation of NiV₂O₆/BiVO₄ with Co-Pi blocks the recombination mediated by the surface states and decreases (increases) significantly k_{rec} (k_{tr}) across the entire potential range (Figure 3.25d and e, respectively). As a result, the overall charge transfer efficiency and PEC performance of the Co-Pi/NiV₂O₆/BiVO₄ photoanode are increased dramatically (Figure 3.25f).

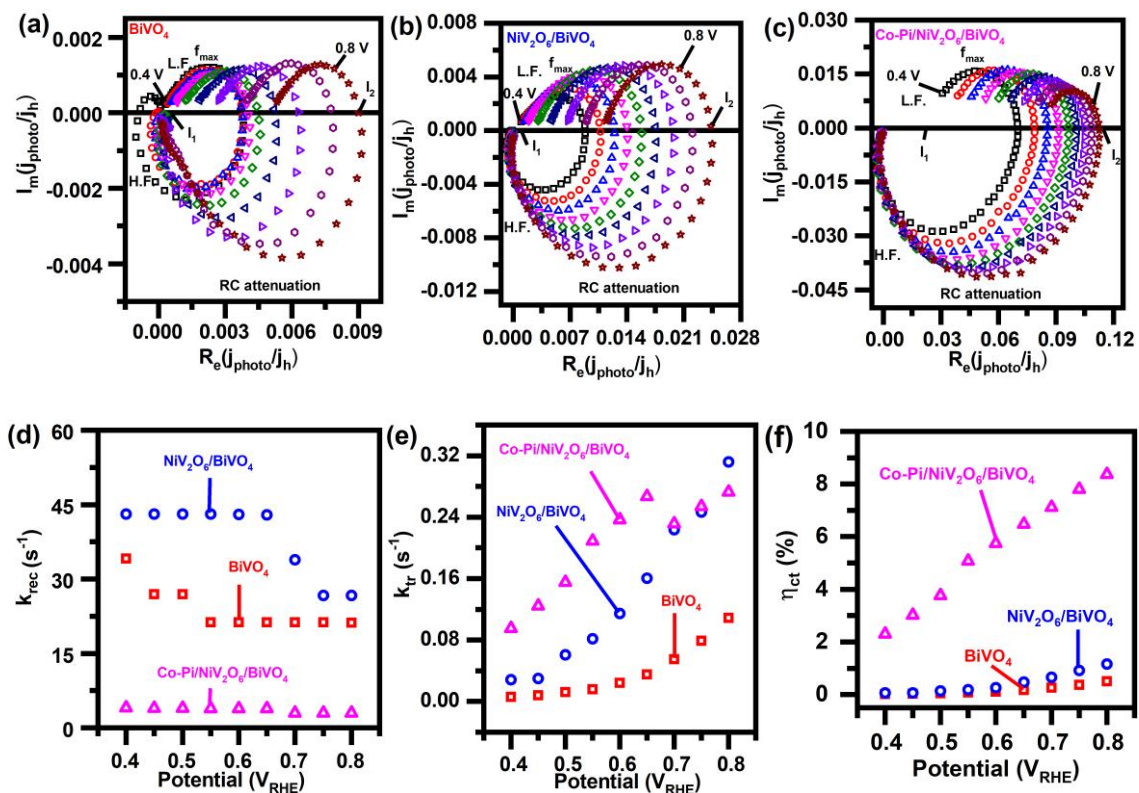


Figure 3.26. Potential dependent IMPS responses for (a) pristine BiVO_4 , (b) $\text{BiVO}_4/\text{NiV}_2\text{O}_6$, (c) $\text{Co-Pi}/\text{NiV}_2\text{O}_6/\text{BiVO}_4$ photoanodes measured in 1.0 M borate buffer solution; and the potential dependence of rate constants of (d) charge recombination (k_{rec}), (e) charge transference (k_{tr}), and (f) charge transfer efficiencies (η_{ct}).

DFT simulations were utilized to explore the electrostatic potential at $\text{NiV}_2\text{O}_6/\text{BiVO}_4$ interfacial contact. Initially, bulk calculations were performed to analyze the electronic structure of BiVO_4 and NiV_2O_6 crystals. The purpose of these calculations was to validate the use of the DFT+U approach in accurately describing the electronic properties of these materials. BiVO_4 exhibits various morphologies, with the monoclinic clinobisvanite phase being the most thermodynamically stable ($a=b=5.15$ Å, and $c=11.72$ Å)[185], with favorable photoelectrochemical properties.[186] The bandgap of BiVO_4 falls within the range of 2.4 to 2.5 eV.[187, 188] By performing volume geometric relaxations on the BiVO_4 unit cell, the lattice parameters were optimized to values very close to the experimental ones: $a=b=5.19$ Å and $c=11.72$ Å. The application of DFT+U predicted an

indirect bandgap of 2.30 eV, demonstrating an excellent agreement with the experimental data. Likewise, the crystal structure of NiV_2O_6 was optimized which displays experimental lattice constants of $a=7.13 \text{ \AA}$, $b=4.79 \text{ \AA}$, and $c=8.83 \text{ \AA}$. [189] Dang et al. reported an indirect bandgap of 2.13 eV for NiV_2O_6 , which aligns well with our findings⁵⁰. The optimized unit cell of NiV_2O_6 displays lattice constants that closely match the experimental values; $a=7.24 \text{ \AA}$, $b=4.86 \text{ \AA}$, and $c=8.92 \text{ \AA}$. Regarding the bandgap, our calculations yielded a value of 2.10 eV, exhibiting excellent agreement with the experimental bandgap. [190] The DFT+U approach effectively reproduces the experimental geometric and electronic bandgaps of both structures. The band edge structures of both BiVO_4 and NiV_2O_6 exhibit a similar pattern (Figure 3.27): the valence band is primarily dominated by the 2p states of oxygen, while the conduction band is dominated by the 3d states of vanadium.

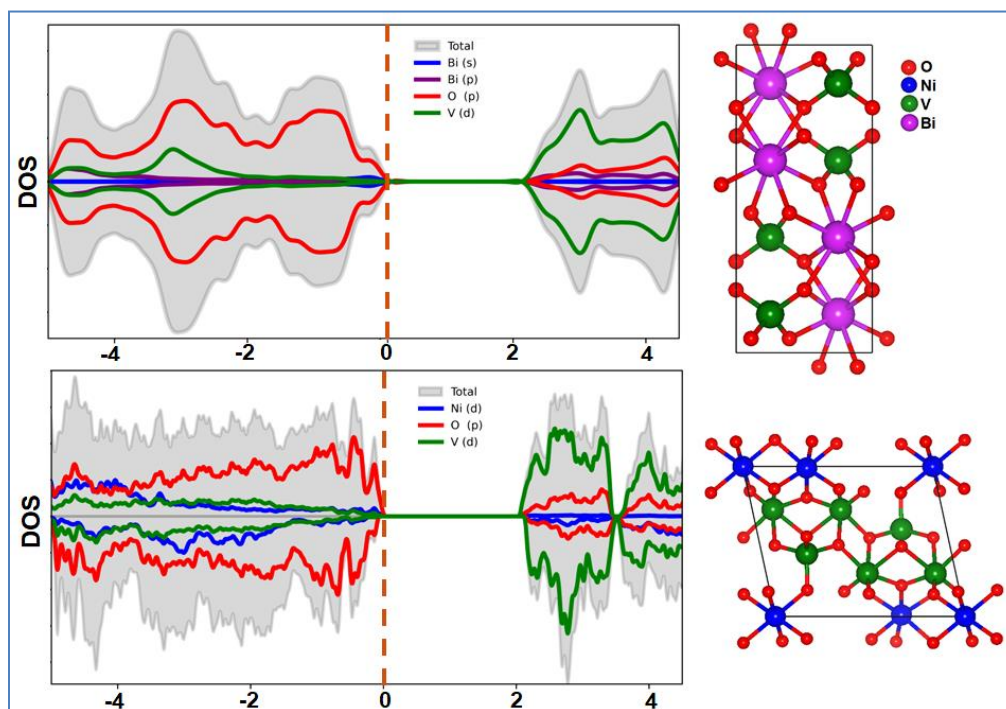


Figure 3.27. The density of states (DOS) and the partial DOS of BiVO_4 and NiV_2O_6 structures. The molecular representation of the unit cells of both structures is shown.

To assess the electrostatic potential at the interface between NiV_2O_6 and BiVO_4 , DFT calculations were performed along two stable facets, namely (001) and (110), to determine

the evolution of the electrostatic potential along the interfacial plane. Figure 3.28 illustrates the planar electrostatic potential (depicted in black) and its average along the crystal c-axis (depicted in red), which is perpendicular to the interfacial plane. For the two facets, BiVO_4 exhibited on average more negative electrostatic potential than that of NiV_2O_6 . The electrostatic potential profile exhibits a sharp change at the interface, with a change of 1.74 V observed for the (110) facet and nearly 4.0 V for the (001) facet. Such a significant change in the electrostatic potential is expected to facilitate the dissociation of the generated excitons at the interface and enhance their diffusion length. Similar findings have been reported by Gao et al. for heterostructures involving transition metal dichalcogenides.[191]

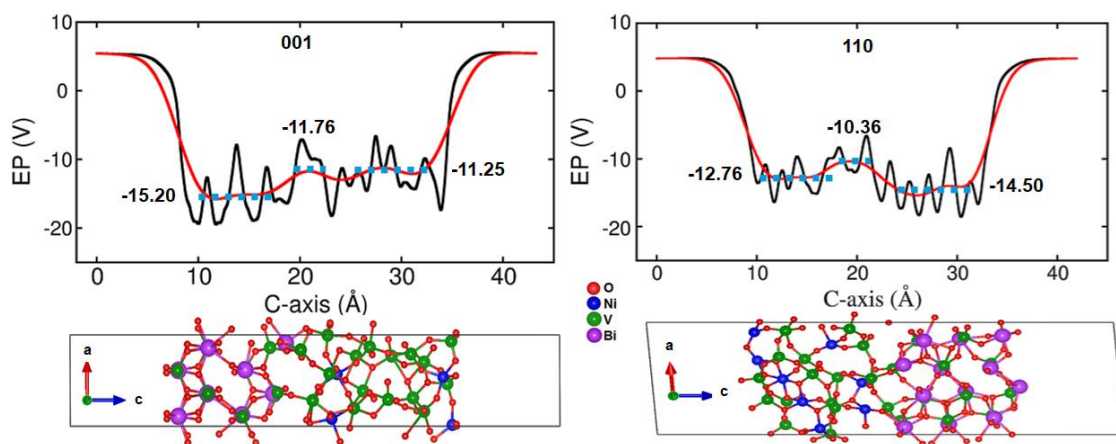


Figure 3.28. Electrostatic potentials (planar along the C-axis (black) and its average (red)) along the interfacial axis of the $\text{NiV}_2\text{O}_6/\text{BiVO}_4$ heterostructure. Lower panel molecular models of the heterostructures along (001), and (110) facets.

Further, Buchaca-Domingo et al.[192] reported a direct correlation between the charge transfer state and the interfacial area between donor/acceptor for the polymer-fullerene photovoltaic systems. The authors mentioned that there is an optimal interfacial area that could minimize the recombination and enhance the exciton diffusion. The steep change in electrostatic potential at the $\text{NiV}_2\text{O}_6/\text{BiVO}_4$ interface, predicted by DFT, is expected to significantly affect charge separation and transport. The sudden change creates a strong

built-in electric field at the back-contact side, hindering back recombination and directing photogenerated electrons toward the NiV_2O_6 back contact layer due to its more positive electrostatic potential. Conversely, the photogenerated holes will move towards the BiVO_4 top layer due to its higher negative electrostatic potential compared to NiV_2O_6 . Consequently, the back-surface recombination will be minimized, and hole diffusion length will be improved, which is consistent with the experimental observations.

3.4. CoV₂O₆/BiVO₄ heterostructured Photoanodes

To avoid the formation of pine holes and block the plausible back-reduction reaction at the FTO layer, we have developed a facile two-step strategy to fabricate CoV₂O₆/BiVO₄ photoanode. The Co(OH)₂ film was grown on the FTO substrate, and subsequently, this layer was used as a sacrificial layer to form the CoV₂O₆/BiVO₄ heterostructure. Figs. 3.29(a-d) shows the SEM images of Co(OH)₂, pristine BiVO₄, CoV₂O₆/BiVO₄ heterostructure, and Co-Pi/CoV₂O₆/BiVO₄ photoanodes. It is observed from Figure 3.29a that the Co(OH)₂ layer has a flower-like morphology consisting of thin fused rose petals. These fused petals are homogeneously and continuously grown on the FTO substrate. Figure 3.29b shows the pristine BiVO₄ grown directly on the FTO substrate. It has a discontinuous layer and has peanut-like nanoparticles that are aggregated and leave behind cracks. Due to this discontinuous layer formation, the pristine BiVO₄ photoanode shows a very low PEC activity, which could be due to the back-reduction reaction.[193] In the presence of the Co(OH)₂ layer, a continuous CoV₂O₆/BiVO₄ heterostructure was readily formed (Figure 3.29c). For clarity, the low and high magnification images of pristine BiVO₄ and CoV₂O₆/BiVO₄ are presented in Figure 3.29(b & c), and Figure 3.29c clearly shows the absence of cracks in the CoV₂O₆/BiVO₄ film. Figure 3.29d shows the FE-SEM image of Co-Pi/CoV₂O₆/BiVO₄ modified with Co-Pi co-catalyst. The thickness of pristine BiVO₄ and CoV₂O₆/BiVO₄ photoanodes films were estimated through the cross-sectional FE-SEM analysis and presented in Figs. 3.29e and f, respectively. The thickness of BiVO₄ and CoV₂O₆/BiVO₄ photoanodes was approximately 0.84 and 1.08 μm respectively. Figs. 3.29(g & h) show the low and high-resolution images of CoV₂O₆/BiVO₄. The high-resolution TEM image indicates the formation of CoV₂O₆/BiVO₄ heterostructure. The

lattice fringes of BiVO_4 were observed with an interplanar distance of 0.243 and 0.463 nm corresponding to the (220) and (110) crystal planes[194] and the (110) lattice fringes with a lattice spacing of 0.385 nm demonstrating the presence of crystallinity CoV_2O_6 .[195]

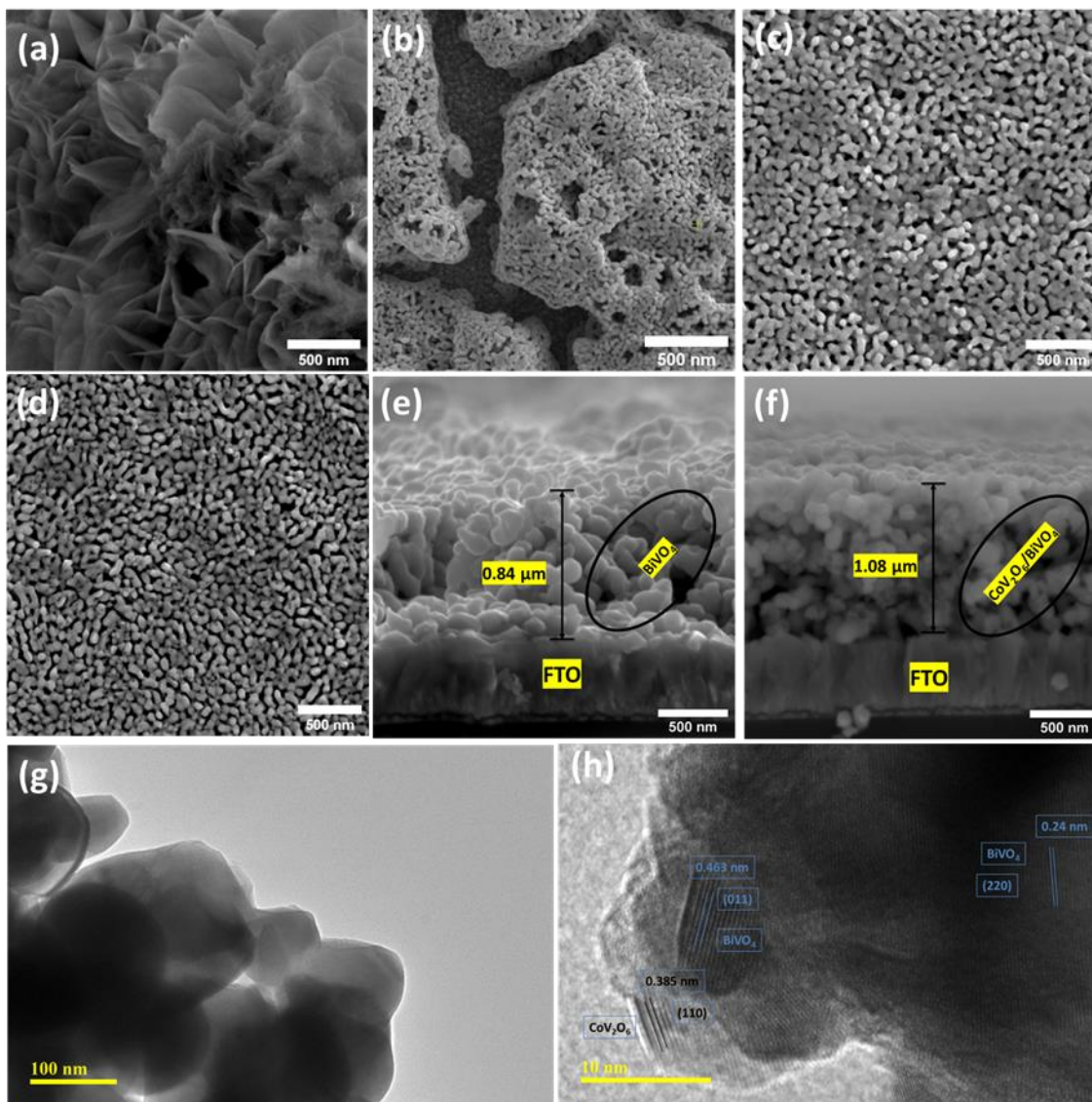


Figure 3.29. Top view FE-SEM images of (a) Co(OH)_2 , (b) pristine BiVO_4 , (c) $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ heterostructure, and (d) $\text{Co-Pi/CoV}_2\text{O}_6/\text{BiVO}_4$ photoanodes, respectively; (g and h) show the low and high-resolution TEM images of $\text{CoV}_2\text{O}_6/\text{BiVO}_4$.

Figure 3.30a shows the X-ray diffraction (XRD) pattern of BiVO_4 , CoV_2O_6 , and $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ photoanodes. The hollow circles (o) represent the XRD peaks of the FTO substrate and appear at 2θ equal to 26.3° , 33.4° , 37.4° , 51.3° , 54.2° , 61.2° , and 65.1° ,

respectively according to JCPDS card no. 041-1445.[26] The diffraction peaks of the BiVO_4 are represented by stars (*) and appear at 2θ equals 18.7° , 28.8° , 30.4° , 35.1° , 39.7° , 42.3° , 47.0° , 50.2° , 53.1° , and 59.2° , respectively. The CoV_2O_6 showed diffraction peaks at 23.35° , 27.56° , 29.73° , 30.82° , 32.85° , 33.81° , 34.98° , 35.96° , 40.01° , and 58.03° according to JCPDS card no. 51-0130.[196] There is no characteristic peak for $\text{Co}(\text{OH})_2$ and CoV_2O_6 observed in the $\text{CoV}_2\text{O}_6/\text{BiVO}_4$, either due to their low concentration and/or amorphous nature[134], but there is little peak shifting for the BiVO_4 (121) peak towards the lower angle. This might be due to internal stress generated during the formation of $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ heterostructure (see inset Figure 3.30a). Figure 3.30b shows the Raman spectra of pristine BiVO_4 , CoV_2O_6 , and $\text{CoV}_2\text{O}_6/\text{BiVO}_4$. The typical Raman peaks of BiVO_4 (CoV_2O_6) at 218, 330, 371, 712, and 831cm^{-1} (138, 194, 283, 398, 570, 698, 862cm^{-1}) have been observed.[197] By comparison, it is obvious that the Raman spectrum of $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ photoanodes exhibits the scattering peaks of both BiVO_4 and CoV_2O_6 with little shifting for the peaks appearing at 136, 145, 288, 575, and 865cm^{-1} . [163] This results in conjugation with the TEM analysis inferred the formation of $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ heterostructure. Figure 3.30c shows the UV-Vis diffuse reflectance spectra of the developed photoanodes. The optical band gap energies of all photoanodes are estimated from the Tauc plots presented in Figure 3.30d. The pristine and Co-Pi modified $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ photoanodes have the same energy band gap of 2.39 eV, which is less than the pristine BiVO_4 (2.50 eV) and higher than that of CoV_2O_6 (2.28 eV).[198]

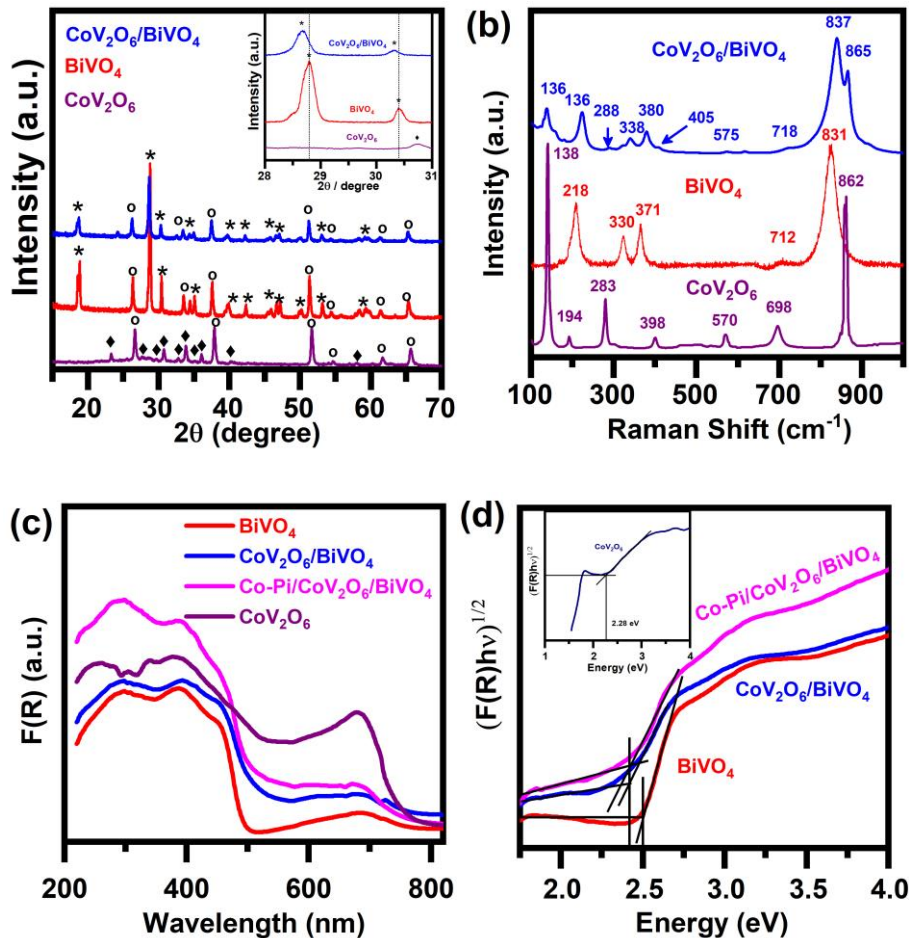


Figure 3.30. (a & b) XRD patterns and Raman spectra of pristine BiVO₄, CoV₂O₆, and CoV₂O₆/BiVO₄ photoanodes, respectively; and (c & d) DRS spectra and Tauc's plot of BiVO₄, CoV₂O₆, CoV₂O₆/BiVO₄, and Co-Pi/CoV₂O₆/BiVO₄ photoanodes, respectively.

The existence of cobalt in the CoV₂O₆/BiVO₄ photoanode was further confirmed by XPS analysis. Figure 3.31 shows the ultra-high-vacuum Al K α spectrum of Bi 4f, Co 2p, V 2p, and O 1s of the CoV₂O₆/BiVO₄ photoanodes. For comparison, the XPS spectra of BiVO₄ were also included. The two high-intensity peaks observed in Figure 3.31a with binding energies of 164.14 eV and 158.92 eV are the splitting signals of 4f_{5/2} and 4f_{7/2} orbitals respectively, which are the characteristic peaks of Bi³⁺.^[199] The Co 2p_{3/2} and Co 2p_{1/2} peaks observed in Figure 3.31b (Co 2p XPS spectrum) at 795.60 eV and 780.24 eV and the two satellite peaks indicated that cobalt is present in a +2-oxidation state in the

CoV₂O₆/BiVO₄. [200] Furthermore, Figure 3.31c shows V 2p XPS spectra of the 2p_{1/2} and 2p_{3/2} orbitals, and their characteristic peaks are observed at 523.92 eV and 516.48 eV, respectively, indicating that V is present in +5 oxidation state. [201]

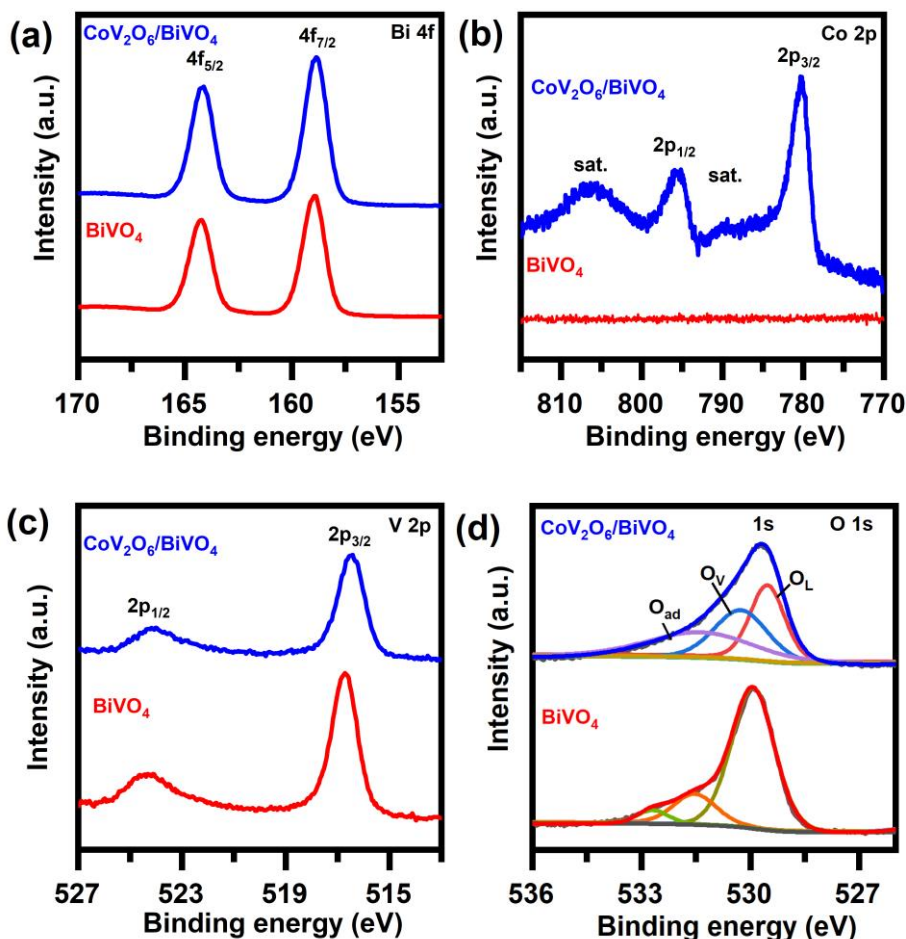


Figure 3.31. XPS spectra of (a) Bi 4f, (b) Co 2p, (c) V 2p, and (d) O 1s of the pristine BiVO₄ and CoV₂O₆/BiVO₄ photoanodes.

The O 1s spectrum of pristine BiVO₄ and CoV₂O₆/BiVO₄ can be deconvoluted into three peaks (Figure 3.31d), the first observed at 529.56 eV corresponds to lattice oxygen (O_L), the second corresponds to the linkage of metal cations in the oxygen-deficient region (O_v), and the third peak is associated with chemisorbed or dissociated oxygen species (O_c) such as adsorbed H₂O. [202]

The PEC performance of the fabricated photoanodes is checked under simulated sunlight irradiation using 1.0 M borate buffer (pH 9.0) as an electrolyte (after pH optimization Figure 3.32a). Figure 3.32b shows the influence of the Co(OH)_2 chemical deposition time on the PEC performance of $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ photoanodes. It was found that 30 min deposition time is optimum. Figure 3.32c shows the photocurrent densities at 1.23 V_{RHE} measured in the presence and absence of Na_2SO_3 for the $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ photoanodes fabricated using different atomic ratios of Bi in the drop-casting solution. This graph shows that the maximum photocurrent is delivered by the $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ photoanode fabricated using a drop-casting solution containing 45 at% Bi and 55 at% V. The maximum photocurrent achieved is 2.35 mA/cm^2 without and 4.65 mA/cm^2 with hole scavenger Na_2SO_3 , respectively. So, this optimized photoanode is utilized for further measurements. Figure 3.32d presents the comparison of photocurrents of pristine BiVO_4 and $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ photoanodes with and without Na_2SO_3 in 1.0 M borate buffer. It is observed from Figure 3.32d that there is approximately a 2-fold enhancement in photocurrent in a buffer solution containing Na_2SO_3 . Figure 3.32e represents the Linear Sweep Voltammograms (LSVs) of pristine BiVO_4 , $\text{CoV}_2\text{O}_6/\text{BiVO}_4$, $\text{Co-Pi}/\text{BiVO}_4$, and $\text{Co-Pi}/\text{CoV}_2\text{O}_6/\text{BiVO}_4$ photoanodes under dark and one sun illumination. Under dark conditions, the photocurrent of all photoanodes is zero, which indicates that there is no reaction under dark. However, we observe a $\text{V}^{4+}/\text{V}^{5+}$ redox peak at 0.4 V_{RHE} (see Figure 3.32f). [52] The intensity of this redox peak is decreased after deposition of Co-Pi on $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ heterostructured photoanode due to the passivation effect of Co-Pi cocatalyst. [52] Under light illumination pristine BiVO_4 displayed 0.43 mA/cm^2 photocurrent. After the formation of $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ heterostructure, the photocurrent is

approximately 6-fold enhanced (2.35 mA/cm^2) as compared to pristine BiVO_4 . After the deposition of co-catalyst Co-Pi on $\text{CoV}_2\text{O}_6/\text{BiVO}_4$, the photocurrent of optimized Co-Pi/ $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ photoanode is further enhanced to 4.22 mA/cm^2 (Figure 3.32g), which is 2 and 10 times higher than that of $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ and pristine BiVO_4 photoanodes, respectively. The enhancement in the photocurrent is further verified by incident photon-to-current conversion efficiency (IPCE) and is presented in Figure 3.32h. There is a significant enhancement in the IPCE value of the Co-Pi/ $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ photoanode (59% at 420 nm) as compared to $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ and pristine BiVO_4 photoanodes at $1.23 \text{ V}_{\text{RHE}}$. To further evaluate the overall water-splitting efficiency, the photoanodes' applied bias photon-to-current efficiency (ABPE) is shown in Figure 3.32i and calculated according to equation 2.1 assuming Faradaic efficiency is equal to 1. The Co-Pi/ $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ photoanode exhibited a 1.45 % ABPE value. This value is 1.5 and 7.0-fold higher than that of $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ (i.e., 0.91%) and pristine BiVO_4 (i.e., 0.23%), respectively. The enhancement in ABPE value after the deposition of Co-Pi on $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ photoanode is usually attributed to the reduction of the surface recombination and acceleration of water oxidation kinetics.[27] The Co-Pi/ $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ photoanode shows excellent stability measured chronoamperometrically at $0.6 \text{ V}_{\text{RHE}}$ for 24 hours and presented in Figure 3.33a. There is only a 7% decrease in photocurrent after 24 hours. To assess the Faradaic efficiency of water oxidation of the Co-Pi/ $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ photoanode, a PEC test (Figure 3.33b) was performed using a sealed PEC cell at $1.23 \text{ V}_{\text{RHE}}$. The cell was connected online with a gas chromatograph (GC) to quantify the amount of the evolved H_2 and O_2 gases. A Faradaic efficiency of 95 % was achieved (Figure 3.33c).

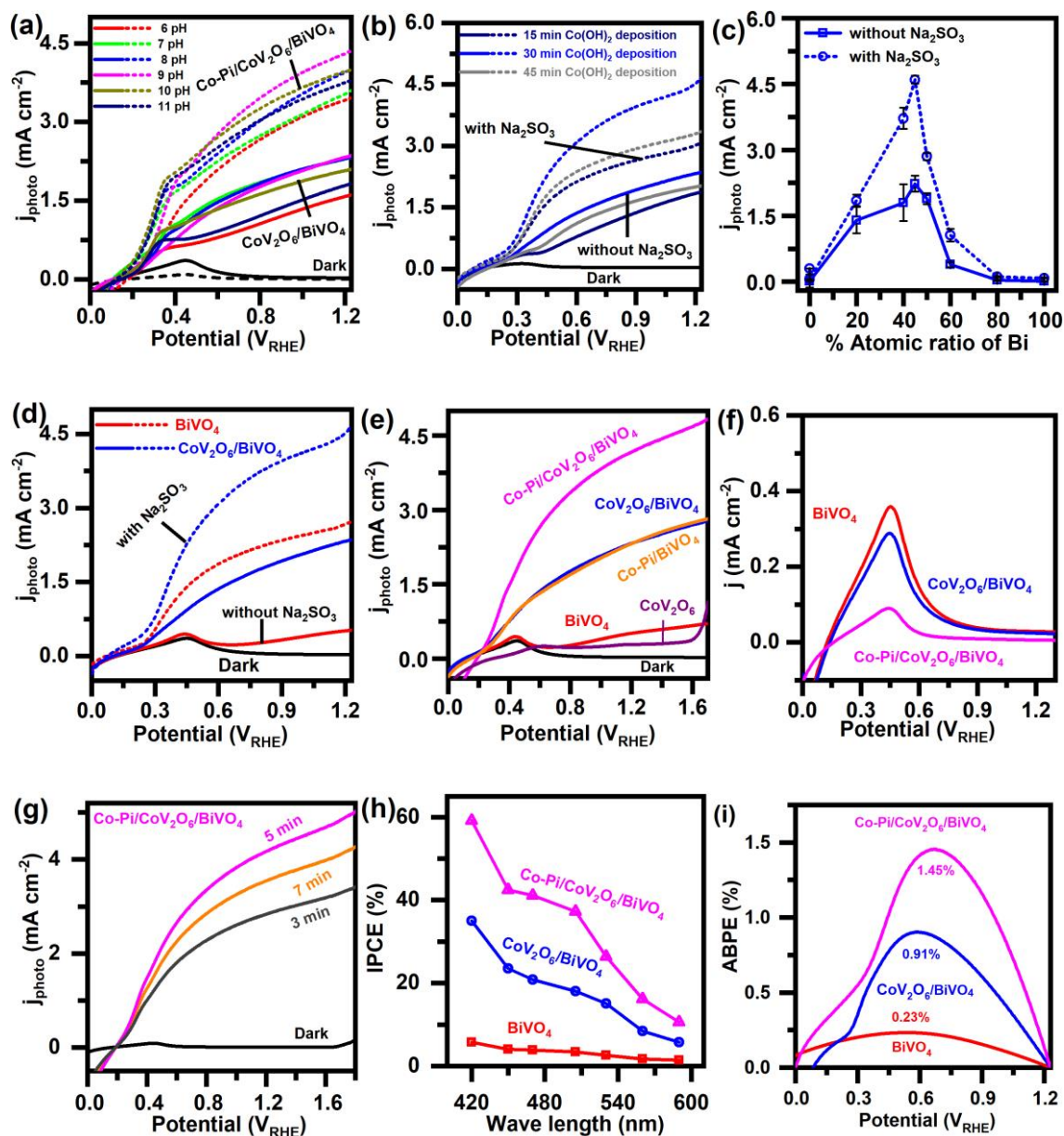


Figure 3.32. LSVs of (a) $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ and $\text{Co-Pi}/\text{CoV}_2\text{O}_6/\text{BiVO}_4$ photoanodes in different pH borate buffers, (b) $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ photoanode in borate buffer with and without Na_2SO_3 at different deposition times of $\text{Co}(\text{OH})_2$ on FTO substrate, (c) Photocurrent densities of $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ photoanodes at 1.23 V_{RHE} with different atomic ratio Bi^{3+} ion solution on $\text{Co}(\text{OH})_2$ layer in borate buffer with and without hole scavenger Na_2SO_3 ; (d) LSVs of pristine BiVO_4 and optimized $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ photoanodes with and without Na_2SO_3 . (e) LSVs for pristine BiVO_4 , CoV_2O_6 , $\text{CoV}_2\text{O}_6/\text{BiVO}_4$, and $\text{Co-Pi}/\text{CoV}_2\text{O}_6/\text{BiVO}_4$ photoanodes. (f) LSVs of photoanodes in dark, (g) LSVs for optimization of Co-Pi deposition time, (h) IPCE % of pristine BiVO_4 , $\text{CoV}_2\text{O}_6/\text{BiVO}_4$, and $\text{Co-Pi}/\text{CoV}_2\text{O}_6/\text{BiVO}_4$ photoanodes, and (i) The ABPE of pristine BiVO_4 , $\text{CoV}_2\text{O}_6/\text{BiVO}_4$, and $\text{Co-Pi}/\text{CoV}_2\text{O}_6/\text{BiVO}_4$ photoanodes for PEC water splitting. Conditions: 100 mW cm^{-2} with AM 1.5 G filter (a-e, g, and i) and monochromatic light (h); electrolyte: 1.0 M borate buffer solution with pH 9.0.

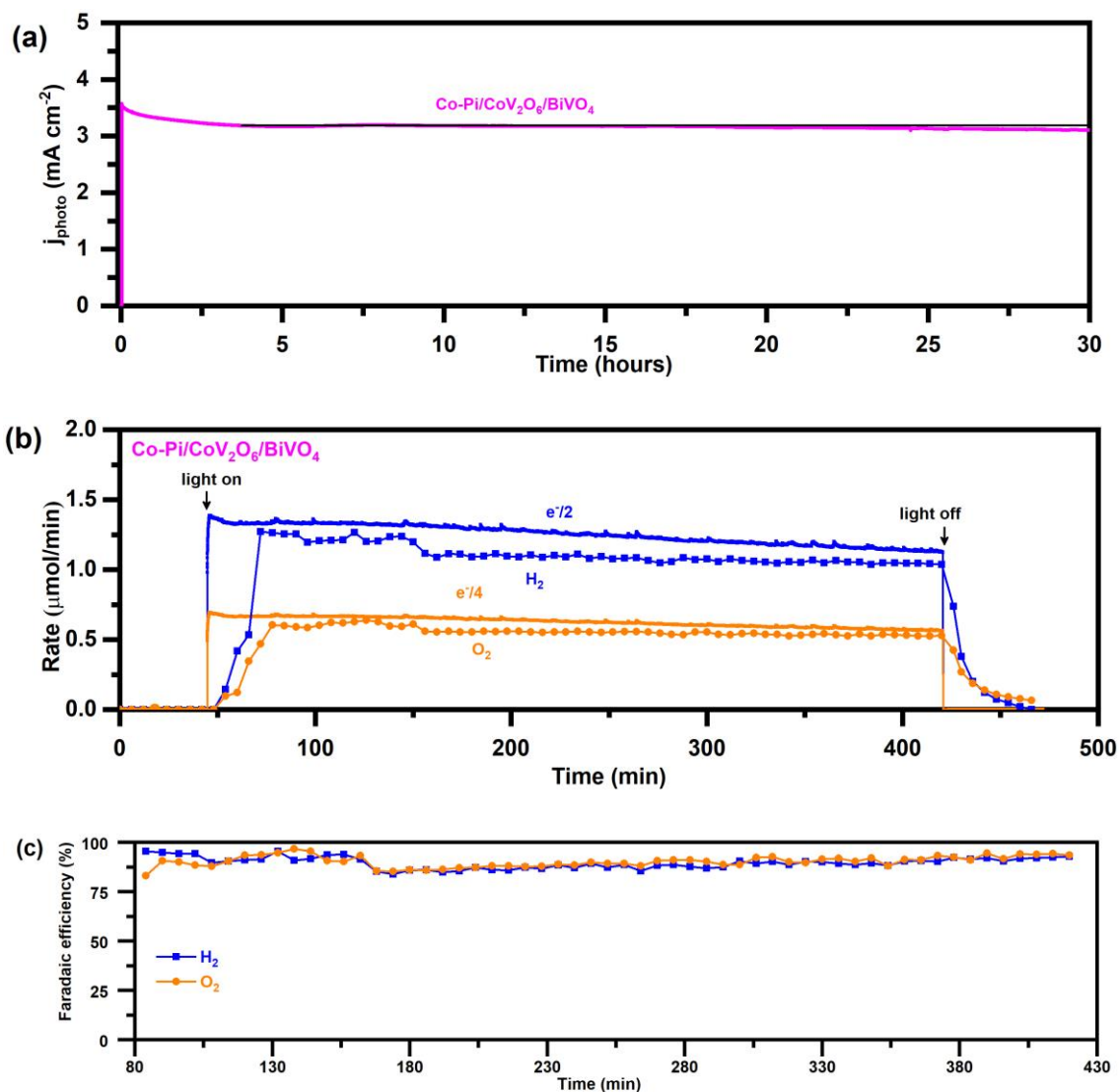


Figure 3.33. (a) The Chronoamperometrically stability test of Co-Pi/CoV₂O₆/BiVO₄ photoanode at 0.6 V_{RHE} (b) Rate of H₂ and O₂ produced from the amount of photocurrent produced and from GC at 1.23 V_{RHE} for Co-Pi/CoV₂O₆/BiVO₄ photoanode in 1.0 M borate buffer having pH=9.0 and (c) shows the respective Faradaic efficiencies.

To explore the effect of CoV₂O₆/BiVO₄ heterostructure formation on the lifetime of the photogenerated holes, the transient photocurrent (TPC) decay upon illumination is measured and presented in Figure 3.34a. The lifetime was estimated as the time at which $\ln(D) = -1$, where the parameter D is determined from equation 3.1 and presented in Fig 6b:[26] The transient decay times estimated from Figure 3.34b for BiVO₄, Co-Pi/BiVO₄, CoV₂O₆/BiVO₄, and Co-Pi/CoV₂O₆/BiVO₄ photoanodes are 0.26, 1.50, 1.45, and 2.20 s,

respectively. These values indicated that there is an approximately 5-fold enhancement in the transient decay time after the formation of $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ heterostructure and a 9-fold enhancement after Co-Pi deposition on $\text{CoV}_2\text{O}_6/\text{BiVO}_4$. This indicates that the $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ heterostructure formation significantly suppresses the surface recombination and prolongs the minority carriers' lifetime. The prolonged minority carriers' lifetime and reduced recombination should result in an improved photovoltage. Indeed, the measured transient open circuit potential (OCP) in the dark and light illumination showed a significant improvement in the generated photovoltage ($V_{\text{ph}} = \text{OCP}_{\text{light}} - \text{OCV}_{\text{dark}}$), see Figure 3.34c.

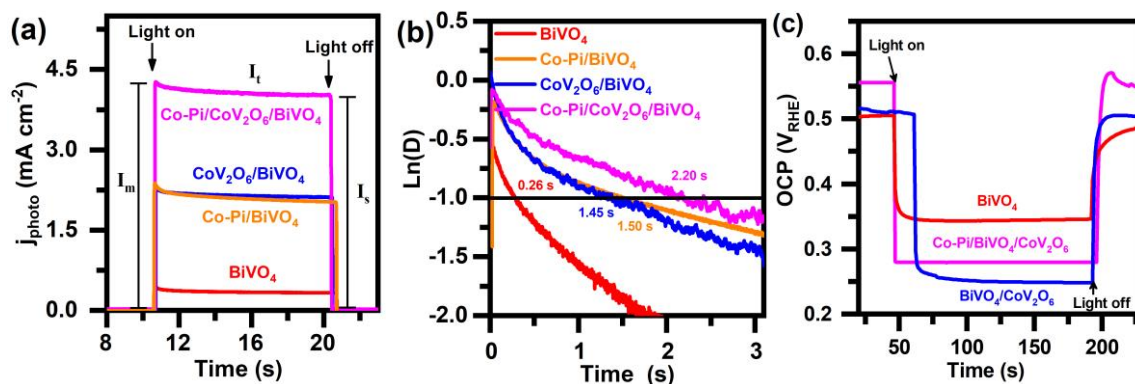


Figure 3.34. (a) Transient photocurrent (TPC), (b) Transient decay times, and (c) OCP curves of BiVO_4 , Co-Pi/BiVO_4 , $\text{CoV}_2\text{O}_6/\text{BiVO}_4$, and $\text{Co-Pi/CoV}_2\text{O}_6/\text{BiVO}_4$ photoanodes. Parts (a) and (b) were measured at 1.23 V_{RHE} .

So far, the improved PEC performance of $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ is mainly due to the prolonged hole lifetime and the reduced surface recombination. To further affirm this conclusion, the rate constants for charge transfer (k_{tr}) and recombination (k_{rec}) at the $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ surface were determined from the intensity-modulated photocurrent spectroscopy (IMPS) analysis. According to the general theory of IMPS, as the frequency increases, the relaxation in the concentration of photogenerated at the surface of the photoanode is

characterized by f_{max} (at the apex of the upper semicircle), where $2\pi f_{max} = \omega = k_{tr} + k_{rec}$. [203]

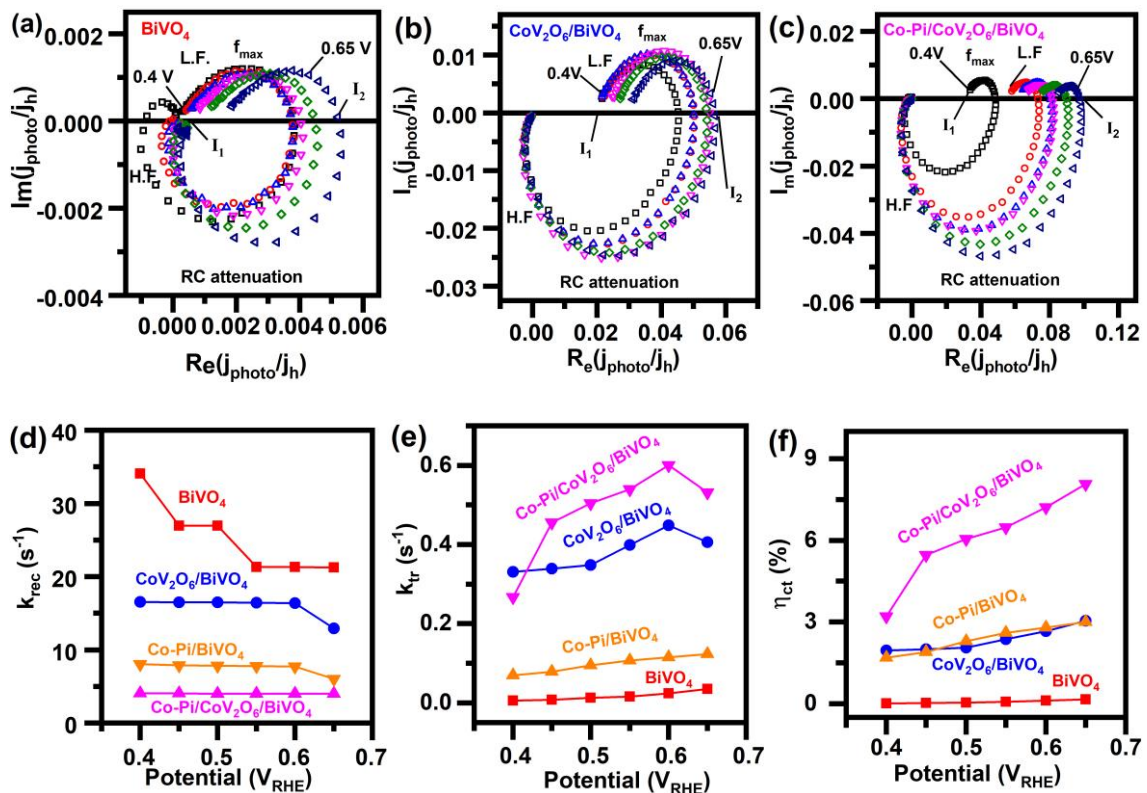


Figure 3.35. IMPS responses of (a) pristine BiVO₄, (b) CoV₂O₆/BiVO₄, (c) Co-Pi/CoV₂O₆/BiVO₄ photoanodes recorded in the potential window from 0.40 to 0.65 V_{RHE} and the corresponding rate constant of (d) charge recombination (k_{rec}), (e) charge transfer (k_{tr}), and (f) charge transfer efficiency.

The charge transfer efficiency (η_{ct}) can be derived from the intersections of the upper semicircle with the real axis at low frequency (I_1), which is equal to $(\eta_{ct}=I_1=k_{tr}/k_{tr} + k_{rec})$. [52] Figure 3.35(a-c) show the IMPS spectra of pristine BiVO₄, CoV₂O₆/BiVO₄ heterostructure, Co-Pi/CoV₂O₆/BiVO₄, and Co-Pi/BiVO₄ photoanodes, respectively. It is observed from Fig. 3.35(d & e) that the CoV₂O₆/BiVO₄ has a lower (higher) k_{rec} (k_{tr}) value than pristine CoV₂O₆/BiVO₄ and the k_{rec} (k_{tr}) was further reduced (enhanced) after loading the CoV₂O₆/BiVO₄ with Co-Pi. Fig. 3.35f shows the charge transfer efficiency ($\eta_{ct}=(k_{tr}/(k_{tr} + k_{rec}))$) of CoV₂O₆/BiVO₄ is significantly higher

than that of the pristine BiVO_4 . The Co-Pi loading further improves the charge transfer efficiency due to the passivation and catalysis effect, as reported previously.[52, 204]

The hole transfer between the BiVO_4 and CoV_2O_6 could cause reduced recombination, a prolonged hole lifetime, and eventually improved PEC performance. The band structures of BiVO_4 and CoV_2O_6 have been constructed to examine this possibility. From the Mott-Schottky plot presented in Fig. 3.36a, the flat band potential (V_{fb}) and doping density (N_d) of pristine BiVO_4 and CoV_2O_6 photoanodes were estimated using equations 3 and 4 respectively.[176] Assuming that the flatband potential represents the conduction band minimum (CBM), the valance band maximum (VBM) was set by adding the value of the bandgap obtained from the Tau's plot presented in Fig. 3.30d. Based on this information the band structures of BiVO_4 and CoV_2O_6 have been drawn in Fig. 3.36b. It is obvious from the VBM of BiVO_4 is positioned more positively than that of CoV_2O_6 . Upon illumination, the photogenerated holes in BiVO_4 can thus migrate to the CoV_2O_6 where they might be stored by the oxidation of Co^{2+} into Co^{3+} to store holes for water oxidation process.

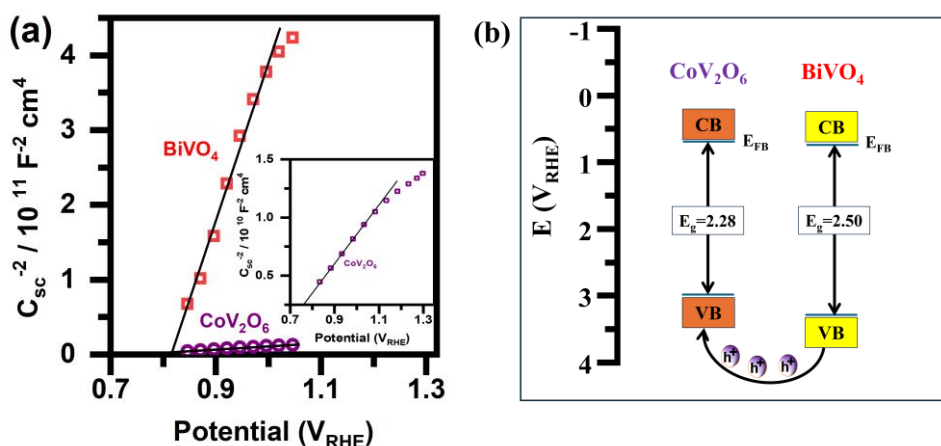


Figure 3.36. (a) Mott-Schottky plots of pristine BiVO_4 , $\text{CoV}_2\text{O}_6/\text{BiVO}_4$, and Co-Pi/ $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ photoanodes, (b) band structure of BiVO_4 and CoV_2O_6 .

4. CONCLUSION & FUTURE RECOMMENDATIONS

BiVO_4 is a promising material with a suitable bandgap (2.4-2.5 eV) to absorb a significant portion of solar light relative to wide-bandgap semiconductors such as TiO_2 . But, it has some drawbacks such as the sluggish water oxidation kinetics on its surface leading to severe charge carrier recombination and thus reducing the overall efficiency. In this thesis, we modified BiVO_4 with CoNi, CoFe, and NiFe-LDHs to passivate the surface states and elongate the transient decay time of photogenerated holes. The CoNi-LDH showed the highest passivation capability and the CoNi-LDH/ BiVO_4 photoanode exhibited the longest transient decay time (3.80 s, 15-fold higher than pristine BiVO_4). The measured photovoltages of BiVO_4 , NiFe-LDH/ BiVO_4 , CoFe-LDH/ BiVO_4 , and CoNi-LDH/ BiVO_4 photoanodes further confirmed that the latter exhibits the best passivation capability. The IMPS studies confirmed fairly that the deposition of CoNi-LDH on BiVO_4 passivates the surface states and unpins the Fermi level. NiFe-LDH and CoFe-LDH passivate the surface of BiVO_4 to a lesser extent and the Fermi level pinning is observed. NiFe-LDH has higher electrocatalytic activity than CoFe-LDH, and CoNi-LDH, but the PEC response of the NiFe-LDH/ BiVO_4 is less than that of CoNi-LDH/ BiVO_4 . This indicates that the overall efficiency is determined by the passivation and catalysis and CoNi-LDH/ BiVO_4 has a dual function.

Pristine BiVO_4 and $\text{Ti}_3\text{C}_2\text{T}_x\text{Mxene}/\text{BiVO}_4$ photoanodes were also fabricated using a novel and facile solution processing method and thoroughly tested for photoelectrochemical water splitting. The charge carrier dynamics in the fabricated photoanodes were investigated using transient open circuit potential (OCP), transient photocurrent (TPC),

photoelectrochemical impedance spectroscopy (PEIS), and intensity-modulated photocurrent spectroscopy (IMPS). It was found that the $\text{Ti}_3\text{C}_2\text{T}_x\text{Mxene}$ acts as a hole transport and/or storage layer between the BiVO_4 surface and the electrolyte. Due to the difference in work function, the $\text{Ti}_3\text{C}_2\text{T}_x\text{Mxene}$ layer forms a Schottky-like junction at the $\text{Ti}_3\text{C}_2\text{T}_x\text{Mxene}/\text{BiVO}_4$ interface and creates a strong built-in electric field that increases the band bending and space charge layer, eventually drifting the photo-generated electrons toward the bulk, whereas the photogenerated electrons are transported via the MXene layer to the electrode/electrolyte interface, where they are utilized for water oxidation. Despite the enhancement by $\text{Ti}_3\text{C}_2\text{T}_x\text{Mxene}$ on the overall efficiency, the IMPS results indicate that $\text{Ti}_3\text{C}_2\text{T}_x\text{Mxene}/\text{BiVO}_4$ exhibits high values for the phenomenological recombination rate constant. This is attributed to the high concentration of holes (stored holes) at the surface and the slow kinetics for water oxidation on the $\text{Ti}_3\text{C}_2\text{T}_x\text{Mxene}$ layer. The modification of the $\text{Ti}_3\text{C}_2\text{T}_x\text{Mxene}/\text{BiVO}_4$ photoanode with an OEC, like Co-Pi, is thus necessary to achieve the full PEC output. Indeed, the Co-Pi/ $\text{Ti}_3\text{C}_2\text{T}_x\text{Mxene}/\text{BiVO}_4$ photoanode showed a current density of 4.72 mA cm^{-2} , which is 11.0 times higher than that of pristine BiVO_4 at $1.23 \text{ V}_{\text{RHE}}$ under standard illumination conditions and among the best-reported values.

A pinhole-free BiVO_4 photoanode with a NiV_2O_6 back contact layer was fabricated using a facile method. A nickel hydroxide layer was grown on the FTO substrate using a chemical bath deposition method and used as a sacrificial layer for the formation of BiVO_4 with NiV_2O_6 back contact (BCI) interfacial layer. This has been readily achieved by drop-casting and heat treatment. The $\text{NiV}_2\text{O}_6/\text{BiVO}_4$ exhibited a 2-fold higher hole diffusion length than pristine BiVO_4 , but still, the high surface recombination limits the PEC performance as confirmed by the intensity-modulated photocurrent spectroscopy. Surface

passivation with Co-Pi was crucial for substantial improvement. The optimized Co-Pi modified photoanode achieved a stable photocurrent density of 4.8 mA cm^{-2} which is 12-fold higher than pristine BiVO_4 . DFT simulations demonstrated a sharp electrostatic potential change at the NiV_2O_6 BCI layer and BiVO_4 interface. The average electrostatic potential on BiVO_4 is more negative than that of NiV_2O_6 and thus a strong built-in electric field is generated at the interface. Such an electric field drifts the photoelectrons toward the back contact (NiV_2O_6 layer) and photogenerated holes toward the front surface (BiVO_4 layer) and thus reduces the back surface recombination and improves the hole diffusion length. This study marks a significant advancement in fabricating bismuth vanadate-based photoanodes with a back contact interfacial layer for improved photoelectrochemical performance.

Using the same approach for $\text{NiV}_2\text{O}_6/\text{BiVO}_4$ synthesis, the $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ heterostructure was successfully fabricated and showed enhanced PEC performance for water oxidation after modification with Co-Pi OEC. The Co-Pi/ $\text{CoV}_2\text{O}_6/\text{BiVO}_4$ photoanode exhibited approximately 10-fold higher photocurrent density than pristine BiVO_4 . The enhancement in photocurrent was attributed to the elongation of the lifetime of the photogenerated holes and the improved charge transfer efficiency as revealed by the TPC and IMPS measurements.

Future Work

In this thesis, a facile and handy protocol has been developed for the fabrication of BiVO_4 photoanodes with photoelectrochemical activity close to the theoretical value. In future work, we aim to investigate the long-term stability of the fabricated electrodes under practical operational conditions. These photoanodes can be integrated with a suitable photocathode to fabricate a bias-free device for PEC water splitting.

References

- [1] L. Bernstein, P. Bosch, O. Canziani, Z. Chen, R. Christ, and K. Riahi, "IPCC, 2007: climate change 2007: synthesis report," ed: IPCC, 2008.
- [2] D. L. Greene, J. L. Hopson, and J. Li, "Have we run out of oil yet? Oil peaking analysis from an optimist's perspective," *Energy policy*, vol. 34, no. 5, pp. 515-531, 2006.
- [3] Q. Meng and R. Bentley, "Global oil peaking: Responding to the case for 'abundant supplies of oil'," *Energy*, vol. 33, no. 8, pp. 1179-1184, 2008.
- [4] S. C. Bhattacharyya, "Concepts, Issues, Markets and Governance," *Energy Economics*, pp. 978-0, 2011.
- [5] I. OECD, "Energy and air pollution: world energy outlook special report 2016," 2016.
- [6] S. M. N. Nawaz and S. Alvi, "Energy security for socio-economic and environmental sustainability in Pakistan," *Heliyon*, vol. 4, no. 10, 2018.
- [7] H. Waisman, J. Rozenberg, O. Sassi, and J.-C. Hourcade, "Peak oil profiles through the lens of a general equilibrium assessment," *Energy Policy*, vol. 48, pp. 744-753, 2012.
- [8] C. M. Suarez, S. Hernández, and N. Russo, "BiVO₄ as photocatalyst for solar fuels production through water splitting: a short review," *Applied Catalysis A: General*, vol. 504, pp. 158-170, 2015.
- [9] J. H. Kim, D. Hansora, P. Sharma, J.-W. Jang, and J. S. Lee, "Toward practical solar hydrogen production—an artificial photosynthetic leaf-to-farm challenge," *Chemical Society Reviews*, vol. 48, no. 7, pp. 1908-1971, 2019.
- [10] Q. Wang and K. Domen, "Particulate photocatalysts for light-driven water splitting: mechanisms, challenges, and design strategies," *Chemical Reviews*, vol. 120, no. 2, pp. 919-985, 2019.
- [11] S. Luo, X. Ren, H. Lin, H. Song, and J. Ye, "Plasmonic photothermal catalysis for solar-to-fuel conversion: current status and prospects," *Chemical Science*, vol. 12, no. 16, pp. 5701-5719, 2021.
- [12] K. Sivula, F. Le Formal, and M. Grätzel, "Solar water splitting: progress using hematite (α -Fe₂O₃) photoelectrodes," *ChemSusChem*, vol. 4, no. 4, pp. 432-449, 2011.
- [13] C. H. Christensen, T. Johannessen, R. Z. Sørensen, and J. K. Nørskov, "Towards an ammonia-mediated hydrogen economy? " *Catalysis Today*, vol. 111, no. 1-2, pp. 140-144, 2006.
- [14] B. Moss, O. Babacan, A. Kafizas, and A. Hankin, "A review of inorganic photoelectrode developments and reactor scale-up challenges for solar hydrogen production," *Advanced Energy Materials*, vol. 11, no. 13, p. 2003286, 2021.
- [15] H. Song, S. Luo, H. Huang, B. Deng, and J. Ye, "Solar-Driven Hydrogen Production: Recent Advances, Challenges, and Future Perspectives," *ACS Energy Letters*, vol. 7, no. 3, pp. 1043-1065, 2022/3// 2022.
- [16] B. Liu *et al.*, "Tandem cells for unbiased photoelectrochemical water splitting," *Chemical Society Reviews*, 2023.

- [17] R. C. Armstrong *et al.*, "The frontiers of energy," *Nature Energy*, vol. 1, no. 1, pp. 1-8, 2016.
- [18] G. Dong, L. Yan, and Y. Bi, "Advanced oxygen evolution reaction catalysts for solar-driven photoelectrochemical water splitting," *Journal of Materials Chemistry A*, vol. 11, no. 8, pp. 3888-3903, 2023.
- [19] M. Tayebi and B.-K. Lee, "Recent advances in BiVO₄ semiconductor materials for hydrogen production using photoelectrochemical water splitting," *Renewable and Sustainable Energy Reviews*, vol. 111, pp. 332-343, 2019/9// 2019.
- [20] B. Lamm, B. J. Trzesniewski, H. Doscher, W. A. Smith, and M. Stefik, "Emerging postsynthetic improvements of BiVO₄ photoanodes for solar water splitting," *ACS Energy Letters*, vol. 3, no. 1, pp. 112-124, 2017.
- [21] B. A. Pinaud *et al.*, "Technical and economic feasibility of centralized facilities for solar hydrogen production via photocatalysis and photoelectrochemistry," *Energy & Environmental Science*, vol. 6, no. 7, pp. 1983-2002, 2013.
- [22] K. Sivula and R. Van De Krol, "Semiconducting materials for photoelectrochemical energy conversion," *Nature Reviews Materials*, vol. 1, no. 2, pp. 1-16, 2016.
- [23] J. Sun, D. K. Zhong, and D. R. Gamelin, "Composite photoanodes for photoelectrochemical solar water splitting," *Energy & Environmental Science*, vol. 3, no. 9, pp. 1252-1261, 2010.
- [24] Q. Huang, Z. Ye, and X. Xiao, "Recent progress in photocathodes for hydrogen evolution," *Journal of Materials Chemistry A*, vol. 3, no. 31, pp. 15824-15837, 2015.
- [25] Q. Li *et al.*, "Highly Efficient Visible-Light-Driven Photocatalytic Hydrogen Production of CdS-Cluster-Decorated Graphene Nanosheets," *Journal of the American Chemical Society*, vol. 133, no. 28, pp. 10878-10884, 2011/7// 2011.
- [26] A. Z. Khan, T. A. Kandiel, S. Abdel-Azeim, T. N. Jahangir, and K. Alhooshani, "Phosphate ions interfacial drift layer to improve the performance of CoFe-Prussian blue hematite photoanode toward water splitting," *Applied Catalysis B: Environmental*, vol. 304, p. 121014, 2022.
- [27] A. Z. Khan, T. A. Kandiel, S. Abdel-Azeim, and K. Alhooshani, "Boosting the efficiency of water oxidation via surface states on hematite photoanodes by incorporating Bi³⁺ ions," *Sustainable Energy & Fuels*, vol. 4, no. 8, pp. 4207-4218, 2020.
- [28] T. N. Jahangir, A. Z. Khan, T. A. Kandiel, and B. M. El Ali, "Insights into the charge transfer kinetics in BiVO₄ photoanodes modified with transition metal-based oxygen evolution electrocatalysts," *Catalysis Today*, vol. 413, p. 113918, 2023.
- [29] I. Khan, A. Z. Khan, A. Sufyan, M. Y. Khan, S. I. Basha, and A. Khan, "Ultrasonically controlled growth of monodispersed octahedral BiVO₄ microcrystals for improved photoelectrochemical water oxidation," *Ultrasonics Sonochemistry*, vol. 68, p. 105233, 2020.
- [30] C. Hao *et al.*, "Efficient charge transfer and separation of TiO₂@ NiCo-LDH core-shell nanowire arrays for enhanced photoelectrochemical water-splitting," *Journal of Solid State Electrochemistry*, vol. 23, pp. 2343-2353, 2019.

- [31] H. W. Jeong *et al.*, "Optical resonance and charge transfer behavior of patterned WO₃ microdisc arrays," *Energy & Environmental Science*, vol. 9, no. 10, pp. 3143-3150, 2016.
- [32] Y. Chen *et al.*, "Polarization-Enhanced direct Z-scheme ZnO-WO_{3-x} nanorod arrays for efficient piezoelectric-photoelectrochemical Water splitting," *Applied Catalysis B: Environmental*, vol. 259, p. 118079, 2019.
- [33] Y. Wang *et al.*, "CuO@CoFe layered double hydroxide core-shell heterostructure as an efficient water oxidation electrocatalyst under mild alkaline conditions," *Inorganic Chemistry*, vol. 59, no. 14, pp. 9491-9495, 2020.
- [34] J. Safaei *et al.*, "Enhanced photoelectrochemical performance of Z-scheme g-C₃N₄/BiVO₄ photocatalyst," *Applied Catalysis B: Environmental*, vol. 234, pp. 296-310, 2018.
- [35] A. G. Tamirat, J. Rick, A. A. Dubale, W.-N. Su, and B.-J. Hwang, "Using hematite for photoelectrochemical water splitting: a review of current progress and challenges," *Nanoscale horizons*, vol. 1, no. 4, pp. 243-267, 2016.
- [36] Y. Li, Z. Li, C. Xu, S. Yu, and Z. Sun, "Facile preparation of nickel phosphide for enhancing the photoelectrochemical water splitting performance of BiVO₄ photoanodes," *RSC advances*, vol. 13, no. 12, pp. 8374-8382, 2023.
- [37] J. Wang *et al.*, "Unconventional substitution for BiVO₄ to enhance photoelectrocatalytic performance by accelerating polaron hopping," *ACS Applied Materials & Interfaces*, vol. 15, no. 11, pp. 14359-14368, 2023.
- [38] Y. Peng, P. Zhai, Y. Shi, H. Jiang, and G. Li, "Band alignment and photocatalytic activity of monoclinic BiVO₄ (0 1 0) and (1 0 0) films with SrTiO₃," *Applied Surface Science*, vol. 618, pp. 156482-156482, 2023/5// 2023.
- [39] T. W. Kim and K.-S. Choi, "Nanoporous BiVO₄ photoanodes with dual-layer oxygen evolution catalysts for solar water splitting," *Science*, vol. 343, no. 6174, pp. 990-994, 2014.
- [40] Q. Shi *et al.*, "Role of tungsten doping on the surface states in BiVO₄ photoanodes for water oxidation: tuning the electron trapping process," *Acs Catalysis*, vol. 8, no. 4, pp. 3331-3342, 2018.
- [41] R. P. Antony *et al.*, "Electrospun Mo-BiVO₄ for efficient photoelectrochemical water oxidation: direct evidence of improved hole diffusion length and charge separation," *Electrochimica Acta*, vol. 211, pp. 173-182, 2016.
- [42] F. F. Abdi, T. J. Savenije, M. M. May, B. Dam, and R. Van De Krol, "The origin of slow carrier transport in BiVO₄ thin film photoanodes: a time-resolved microwave conductivity study," *The Journal of Physical Chemistry Letters*, vol. 4, no. 16, pp. 2752-2757, 2013.
- [43] G. Fang, Z. Liu, and C. Han, "Enhancing the PEC water splitting performance of BiVO₄ co-modifying with NiFeOOH and Co-Pi double layer cocatalysts," *Applied Surface Science*, vol. 515, p. 146095, 2020.
- [44] M. A. Gaikwad *et al.*, "Rapid synthesis of ultrathin Ni: FeOOH with in situ-induced oxygen vacancies for enhanced water oxidation activity and stability of BiVO₄ photoanodes," *ACS Applied Materials & Interfaces*, vol. 15, no. 17, pp. 21123-21133, 2023.
- [45] B. Liu *et al.*, "A BiVO₄ photoanode with a VO_x layer bearing oxygen vacancies offers improved charge transfer and oxygen evolution kinetics in

- photoelectrochemical water splitting," *Angewandte Chemie*, vol. 135, no. 10, p. e202217346, 2023.
- [46] H. S. Han *et al.*, "Boosting the solar water oxidation performance of a BiVO₄ photoanode by crystallographic orientation control," *Energy & Environmental Science*, vol. 11, no. 5, pp. 1299-1306, 2018.
 - [47] X. Yin *et al.*, "High porosity Mo doped BiVO₄ film by vanadium re-substitution for efficient photoelectrochemical water splitting," *Chemical Engineering Journal*, vol. 389, p. 124365, 2020.
 - [48] S. Liu *et al.*, "Tungsten induced defects control on BiVO₄ photoanodes for enhanced solar water splitting performance and photocorrosion resistance," *Applied Catalysis B: Environmental*, vol. 298, p. 120610, 2021.
 - [49] P. M. Rao *et al.*, "Simultaneously efficient light absorption and charge separation in WO₃/BiVO₄ core/shell nanowire photoanode for photoelectrochemical water oxidation," *Nano letters*, vol. 14, no. 2, pp. 1099-1105, 2014.
 - [50] B. Zhang, L. Wang, Y. Zhang, Y. Ding, and Y. Bi, "Ultrathin FeOOH nanolayers with abundant oxygen vacancies on BiVO₄ photoanodes for efficient water oxidation," *Angewandte Chemie International Edition*, vol. 57, no. 8, pp. 2248-2252, 2018.
 - [51] D. K. Lee and K.-S. Choi, "Enhancing long-term photostability of BiVO₄ photoanodes for solar water splitting by tuning electrolyte composition," *Nature Energy*, vol. 3, no. 1, pp. 53-60, 2018.
 - [52] T. A. Kandiel, M. G. Ahmed, and A. Y. Ahmed, "Physical Insights into Band Bending in Pristine and Co-Pi-Modified BiVO₄ Photoanodes with Dramatically Enhanced Solar Water Splitting Efficiency," *The Journal of Physical Chemistry Letters*, vol. 11, no. 13, pp. 5015-5020, 2020/07/02 2020.
 - [53] M. A. Gaikwad, U. P. Suryawanshi, U. V. Ghorpade, J. S. Jang, M. P. Suryawanshi, and J. H. Kim, "Emerging surface, bulk, and interface engineering strategies on BiVO₄ for photoelectrochemical water splitting," *Small*, vol. 18, no. 10, p. 2105084, 2022.
 - [54] A. Fujishima and K. Honda, "Electrochemical photolysis of water at a semiconductor electrode," *nature*, vol. 238, no. 5358, pp. 37-38, 1972.
 - [55] Q. Xu, D. Ma, S. Yang, Z. Tian, B. Cheng, and J. Fan, "Novel g-C₃N₄/g-C₃N₄ S-scheme isotype heterojunction for improved photocatalytic hydrogen generation," *Applied Surface Science*, vol. 495, p. 143555, 2019.
 - [56] Y. Zhang *et al.*, "Engineering BiVO₄ and oxygen evolution cocatalyst interfaces with rapid hole extraction for photoelectrochemical water splitting," *ACS Catalysis*, vol. 13, no. 9, pp. 5938-5948, 2023.
 - [57] Z. Xie, D. Chen, J. Zhai, Y. Huang, and H. Ji, "Charge separation via the synergy of homojunction and electrocatalyst in BiVO₄ for photoelectrochemical water splitting," *Applied Catalysis B: Environmental*, vol. 334, p. 122865, 2023.
 - [58] J. H. Kim and J. S. Lee, "Elaborately modified BiVO₄ photoanodes for solar water splitting," *Advanced Materials*, vol. 31, no. 20, p. 1806938, 2019.
 - [59] K.-Y. Yoon *et al.*, "NiFeOx decorated Ge-hematite/perovskite for an efficient water splitting system," *Nature communications*, vol. 12, no. 1, p. 4309, 2021.

- [60] D. Xu *et al.*, "MOF-derived Co_3O_4 thin film decorated BiVO_4 for enhancement of photoelectrochemical water splitting," *Applied Surface Science*, vol. 491, pp. 497-504, 2019.
- [61] Y. Song *et al.*, "Engineering $\text{MoO}_x/\text{MXene}$ hole transfer layers for unexpected boosting of photoelectrochemical water oxidation," *Angewandte Chemie International Edition*, vol. 61, no. 16, p. e202200946, 2022.
- [62] W. Fang, Y. Lin, R. Xu, and L. Fu, "Boosting photoelectrochemical performance of BiVO_4 photoanode by synergistic effect of $\text{WO}_3/\text{BiVO}_4$ heterojunction construction and NiOOH water oxidation cocatalyst modification," *ACS Applied Energy Materials*, vol. 5, no. 9, pp. 11402-11412, 2022.
- [63] R. Yalavarthi, R. Zbořil, P. Schmuki, A. Naldoni, and Š. Kment, "Elucidating the role of surface states of BiVO_4 with Mo doping and a CoOOH co-catalyst for photoelectrochemical water splitting," *Journal of Power Sources*, vol. 483, p. 229080, 2021.
- [64] R. Yang *et al.*, "Synergistic coupling of CoFe-LDH arrays with NiFe-LDH nanosheet for highly efficient overall water splitting in alkaline media," *Applied Catalysis B: Environmental*, vol. 253, pp. 131-139, 2019.
- [65] P. Yue *et al.*, "Super-hydrophilic CoAl-LDH on BiVO_4 for enhanced photoelectrochemical water oxidation activity," *Applied Catalysis B: Environmental*, vol. 286, pp. 119875-119875, 2021/6// 2021.
- [66] Y. Zhu *et al.*, "Interface engineering of 3D BiVO_4/Fe -based layered double hydroxide core/shell nanostructures for boosting photoelectrochemical water oxidation," *Journal of materials chemistry A*, vol. 5, no. 20, pp. 9952-9959, 2017.
- [67] W. Liu *et al.*, "Amorphous cobalt-iron hydroxide nanosheet electrocatalyst for efficient electrochemical and photo-electrochemical oxygen evolution," *Advanced Functional Materials*, vol. 27, no. 14, p. 1603904, 2017.
- [68] F. Zhao *et al.*, " BiVO_4 photoanode decorated with cobalt-manganese layered double hydroxides for enhanced photoelectrochemical water oxidation," *International Journal of Hydrogen Energy*, vol. 45, no. 56, pp. 31902-31912, 2020/11// 2020.
- [69] S. Bai *et al.*, "Photoanode of LDH catalyst decorated semiconductor heterojunction of BiVO_4/CdS to enhance PEC water splitting efficiency," *International Journal of Hydrogen Energy*, vol. 44, no. 45, pp. 24642-24652, 2019.
- [70] M. K. Mohanta, T. K. Sahu, D. Gogoi, N. R. Peela, and M. Qureshi, "Hexagonal boron nitride quantum dots as a superior hole extractor for efficient charge separation in WO_3 -based photoelectrochemical water oxidation," *ACS Applied Energy Materials*, vol. 2, no. 10, pp. 7457-7466, 2019.
- [71] K. Zhang *et al.*, "Black phosphorene as a hole extraction layer boosting solar water splitting of oxygen evolution catalysts," *Nature communications*, vol. 10, no. 1, p. 2001, 2019.
- [72] E. Kecszenovity *et al.*, "Enhanced photoelectrochemical performance of cuprous oxide/graphene nanohybrids," *Journal of the American Chemical Society*, vol. 139, no. 19, pp. 6682-6692, 2017.
- [73] J. Ran, G. Gao, F.-T. Li, T.-Y. Ma, A. Du, and S.-Z. Qiao, " Ti_3C_2 MXene co-catalyst on metal sulfide photo-absorbers for enhanced visible-light photocatalytic

- hydrogen production," *Nature Communications*, vol. 8, no. 1, pp. 13907-13907, 2017/4// 2017.
- [74] A. VahidMohammadi, J. Rosen, and Y. Gogotsi, "The world of two-dimensional carbides and nitrides (MXenes)," *Science*, vol. 372, no. 6547, p. eabf1581, 2021.
 - [75] P. Liu, J. Yi, R. Bao, and H. Zhao, "Construction of MXene–BiVO₄–FeOOH composite photoanode with ultra-low onset potential: performance, DFT calculation and mechanism," *Materials Today Chemistry*, vol. 23, p. 100747, 2022.
 - [76] X. Yu, T. Wang, W. Yin, and Y. Zhang, "Ti₃C₂ MXene nanoparticles modified metal oxide composites for enhanced photoelectrochemical water splitting," *International Journal of Hydrogen Energy*, vol. 44, no. 5, pp. 2704-2710, 2019/1// 2019.
 - [77] R.-K. Ye *et al.*, "Surface engineering of hematite nanorods by 2D Ti₃C₂-MXene: Suppressing the electron-hole recombination for enhanced photoelectrochemical performance," *Applied Catalysis B: Environmental*, vol. 291, p. 120107, 2021.
 - [78] Y. Li *et al.*, "2D/2D heterostructure of ultrathin BiVO₄/Ti₃C₂ nanosheets for photocatalytic overall Water splitting," *Applied Catalysis B: Environmental*, vol. 285, p. 119855, 2021.
 - [79] W. Bai, Y. Zhou, G. Peng, J. Wang, A. Li, and P. F.-X. Corvini, "Engineering efficient hole transport layer Ferrihydrite-MXene on BiVO₄ photoanodes for photoelectrochemical water splitting: work function and conductivity regulated," *Applied Catalysis B: Environmental*, vol. 315, p. 121606, 2022.
 - [80] X. Xie *et al.*, "Photothermal-Effect-Enhanced Photoelectrochemical Water Splitting in MXene-Nanosheet-Modified ZnO Nanorod Arrays," *ACS Applied Nano Materials*, vol. 5, no. 8, pp. 11150-11159, 2022/8// 2022.
 - [81] G. Yang *et al.*, "A universal strategy boosting photoelectrochemical water oxidation by utilizing MXene nanosheets as hole transfer mediators," *Applied Catalysis B: Environmental*, vol. 297, pp. 120268-120268, 2021/11// 2021.
 - [82] D. N. Nguyen *et al.*, "Core-shell structured MXene@Carbon nanodots as bifunctional catalysts for solar-assisted water splitting," *ACS nano*, vol. 14, no. 12, pp. 17615-17625, 2020.
 - [83] D. Yan, X. Fu, Z. Shang, J. Liu, and H. a. Luo, "A BiVO₄ film photoanode with re-annealing treatment and 2D thin Ti₃C₂T_x flakes decoration for enhanced photoelectrochemical water oxidation," *Chemical Engineering Journal*, vol. 361, pp. 853-861, 2019.
 - [84] Z. Wu, H. Zong, B. Fu, and Z. Zhang, "MXene with controlled surface termination groups for boosting photoelectrochemical water splitting," *Journal of Materials Chemistry A*, vol. 10, no. 46, pp. 24793-24801, 2022.
 - [85] Y. Lin, H. Cai, H. Chen, and H. Luo, "One-pot synthesis of Bi₄V₂O₁₁/BiVO₄ heterostructure with enhanced photocatalytic activity for dye degradation," *Applied Surface Science*, vol. 544, pp. 148921-148921, 2021/4// 2021.
 - [86] W. Xu, W. Tian, L. Meng, F. Cao, and L. Li, "Interfacial Chemical Bond-Modulated Z-Scheme Charge Transfer for Efficient Photoelectrochemical Water Splitting," *Advanced Energy Materials*, vol. 11, no. 8, pp. 2003500-2003500, 2021/2// 2021.

- [87] B. R. Lee *et al.*, "All-solution-processed WO₃/BiVO₄ core-shell nanorod arrays for highly stable photoanodes," *ACS applied materials & interfaces*, vol. 11, no. 22, pp. 20004-20012, 2019.
- [88] S. J. Hong, S. Lee, J. S. Jang, and J. S. Lee, "Heterojunction BiVO₄/WO₃ electrodes for enhanced photoactivity of water oxidation," *Energy & Environmental Science*, vol. 4, no. 5, pp. 1781-1787, 2011.
- [89] B. Xiong *et al.*, "Cu₃Mo₂O₉/BiVO₄ heterojunction films with integrated thermodynamic and kinetic advantages for solar water oxidation," *ACS Sustainable Chemistry & Engineering*, vol. 8, no. 37, pp. 14082-14090, 2020.
- [90] T. S. Dabodiya, T. George, and A. Vadivel Murugan, "Enhanced Solar-Photo (Electro) catalysis of Microwave-Hydrothermal Synthesized BiVO₄, ms-BiVO₄/Reduced Graphene Oxide/Ag₃PO₄ Nanohybrid: Crystalline Phase-Dependent Interfacial Charge Carrier Dynamics," *Energy Technology*, vol. 11, no. 3, p. 2201099, 2023.
- [91] S.-S. Zhu *et al.*, "Cu₂S/BiVO₄ Heterostructure photoanode with extended wavelength range for efficient water splitting," *The Journal of Physical Chemistry C*, vol. 125, no. 29, pp. 15890-15898, 2021.
- [92] Y. Li *et al.*, "Fluorine-doped iron oxyhydroxide cocatalyst: promotion on the WO₃ photoanode conducted photoelectrochemical water splitting," *Applied Catalysis B: Environmental*, vol. 304, pp. 120995-120995, 2022/5// 2022.
- [93] S.-Y. Chen, J.-S. Yang, and J.-J. Wu, "Three-dimensional undoped crystalline SnO₂ nanodendrite arrays enable efficient charge separation in BiVO₄/SnO₂ heterojunction photoanodes for photoelectrochemical water splitting," *ACS Applied Energy Materials*, vol. 1, no. 5, pp. 2143-2149, 2018.
- [94] M. Naguib *et al.*, "One-step synthesis of nanocrystalline transition metal oxides on thin sheets of disordered graphitic carbon by oxidation of MXenes," *Chemical communications*, vol. 50, no. 56, pp. 7420-7423, 2014.
- [95] D. K. Zhong, S. Choi, and D. R. Gamelin, "Near-complete suppression of surface recombination in solar photoelectrolysis by "Co-Pi" catalyst-modified W: BiVO₄," *Journal of the American Chemical Society*, vol. 133, no. 45, pp. 18370-18377, 2011.
- [96] Q. Pan *et al.*, "Boosting charge separation and transfer by plasmon-enhanced MoS₂/BiVO₄ p-n heterojunction composite for efficient photoelectrochemical water splitting," *ACS sustainable chemistry & engineering*, vol. 6, no. 5, pp. 6378-6387, 2018.
- [97] J. Wang *et al.*, "Type-II heterojunction CdIn₂S₄/BiVO₄ coupling with CQDs to improve PEC water splitting performance synergistically," *ACS Applied Materials & Interfaces*, vol. 14, no. 40, pp. 45392-45402, 2022.
- [98] K.-H. Ye *et al.*, "BiOI-BiVO₄ photoanodes with significantly improved solar water splitting capability: p-n junction to expand solar adsorption range and facilitate charge carrier dynamics," *Nano Energy*, vol. 18, pp. 222-231, 2015.
- [99] C. Murugan and A. Pandikumar, "Reinforcement of visible-light harvesting and charge-transfer dynamics of BiVO₄ photoanode via formation of p-n heterojunction with CuO for efficient photoelectrocatalytic water splitting," *ACS Applied Energy Materials*, vol. 5, no. 6, pp. 6618-6632, 2022.

- [100] D. Coelho, J. P. R. Gaudencio, S. A. Carminati, F. W. Ribeiro, A. F. Nogueira, and L. H. Mascaro, "Bi electrodeposition on WO₃ photoanode to improve the photoactivity of the WO₃/BiVO₄ heterostructure to water splitting," *Chemical Engineering Journal*, vol. 399, p. 125836, 2020.
- [101] J. Miao *et al.*, "Supramolecular catalyst with [FeCl₄] unit boosting photoelectrochemical seawater splitting via water nucleophilic attack pathway," *Nature Communications*, vol. 15, no. 1, p. 2023, 2024.
- [102] J. Gil-Rostra, J. Castillo-Seoane, Q. Guo, A. B. n. Jorge Sobrido, A. R. González-Elipe, and A. Borrás, "Photoelectrochemical water splitting with ITO/WO₃/BiVO₄/CoPi multishell nanotubes enabled by a vacuum and plasma soft-template synthesis," *ACS Applied Materials & Interfaces*, vol. 15, no. 7, pp. 9250-9262, 2023.
- [103] L. Yang *et al.*, "BiVO₄ photoelectrodes for unbiased solar water splitting devices enabled by electrodepositing of Cu₂O simultaneously as photoanode and photocathode," *Journal of Alloys and Compounds*, vol. 945, p. 169336, 2023.
- [104] M. G. Lee *et al.*, "Tailored BiVO₄/In₂O₃ nanostructures with boosted charge separation ability toward unassisted water splitting," *Carbon Energy*, vol. 5, no. 6, p. e321, 2023.
- [105] Q. Wang *et al.*, "Elucidating the role of hypophosphite treatment in enhancing the performance of BiVO₄ photoanode for photoelectrochemical water oxidation," *ACS Applied Materials & Interfaces*, vol. 14, no. 23, pp. 26642-26652, 2022.
- [106] T. Wang, H. Pei, Y. Zhang, R. Li, J. Zhang, and T. Peng, "Efficient Strategy for Boosting the Solar-Driven Water Oxidation of the BiVO₄ Photoanode by Using a CuPc Derivative as a Hole Transport Highway," *ACS Applied Energy Materials*, vol. 5, no. 9, pp. 11271-11282, 2022.
- [107] T. Wang, H. Cao, J. Wu, M. Golbon Haghighi, R. Sedghi, and P. Du, "Boosting Photoelectrochemical Water Oxidation Performance of Nanoporous BiVO₄ via Dual Cocatalysts Cobaloxime and Ni-OEC Modification," *The Journal of Physical Chemistry C*, vol. 126, no. 27, pp. 11042-11050, 2022.
- [108] W. Fang, L. Fu, A. Qin, Y. Lin, and R. Xv, "Highly active and self-healing Co-doped BiVO₄ photoanode in borate buffer to enhance charge separation and water oxidation kinetics during photoelectrochemical water splitting," *ACS Applied Energy Materials*, vol. 5, no. 5, pp. 6313-6323, 2022.
- [109] M. Tayebi, Z. Masoumi, B. Seo, C.-S. Lim, H.-G. Kim, and B.-K. Lee, "Efficient and Stable MoO_x@Mo-BiVO₄ Photoanodes for Photoelectrochemical Water Oxidation: Optimization and Understanding," *ACS Applied Energy Materials*, vol. 5, no. 9, pp. 11568-11580, 2022.
- [110] Y. Lu *et al.*, "Boosting charge transport in BiVO₄ photoanode for solar water oxidation," *Advanced Materials*, vol. 34, no. 8, p. 2108178, 2022.
- [111] G. Fang *et al.*, "Promising CoFe-NiOOH ternary polymetallic cocatalyst for BiVO₄-based photoanodes in photoelectrochemical water splitting," *ACS Applied Energy Materials*, vol. 4, no. 4, pp. 3842-3850, 2021.
- [112] G. Fang *et al.*, "CoNiO₂ as a novel water oxidation cocatalyst to enhance PEC water splitting performance of BiVO₄," *Chemical Communications*, vol. 56, no. 64, pp. 9158-9161, 2020.

- [113] J. H. Baek *et al.*, "BiVO₄/WO₃/SnO₂ double-heterojunction photoanode with enhanced charge separation and visible-transparency for bias-free solar water-splitting with a perovskite solar cell," *ACS applied materials & interfaces*, vol. 9, no. 2, pp. 1479-1487, 2017.
- [114] A. C. Lazanas and M. I. Prodromidis, "Electrochemical impedance spectroscopy—a tutorial," *ACS Measurement Science Au*, vol. 3, no. 3, pp. 162-193, 2023.
- [115] H. S. Magar, R. Y. Hassan, and A. Mulchandani, "Electrochemical impedance spectroscopy (EIS): Principles, construction, and biosensing applications," *Sensors*, vol. 21, no. 19, p. 6578, 2021.
- [116] T. A. Kandiel, "Mechanistic investigation of water oxidation on hematite photoanodes using intensity-modulated photocurrent spectroscopy," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 403, p. 112825, 2020.
- [117] E. Ponomarev and L. Peter, "A generalized theory of intensity modulated photocurrent spectroscopy (IMPS)," *Journal of Electroanalytical Chemistry*, vol. 396, no. 1-2, pp. 219-226, 1995.
- [118] N. Mahar, A. Al-Ahmed, and A. A. Al-Saadi, "Synthesis of vanadium carbide MXene with improved inter-layer spacing for SERS-based quantification of anti-cancer drugs," *Applied Surface Science*, vol. 607, p. 155034, 2023.
- [119] X. Xu *et al.*, "Engineering interfaces to steer hole dynamics of BiVO₄ photoanodes for solar water oxidation," *Solar RRL*, vol. 3, no. 11, p. 1900115, 2019.
- [120] G. Kresse and J. Hafner, "Ab initio molecular dynamics for liquid metals," *Physical review B*, vol. 47, no. 1, p. 558, 1993.
- [121] G. Kresse and J. Hafner, "Ab initio molecular-dynamics simulation of the liquid-metal–amorphous-semiconductor transition in germanium," *Physical Review B*, vol. 49, no. 20, p. 14251, 1994.
- [122] P. E. Blöchl, "Projector augmented-wave method," *Physical review B*, vol. 50, no. 24, p. 17953, 1994.
- [123] H. J. Monkhorst and J. D. Pack, "Special points for Brillouin-zone integrations," *Physical review B*, vol. 13, no. 12, p. 5188, 1976.
- [124] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," *Physical review letters*, vol. 77, no. 18, p. 3865, 1996.
- [125] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. Humphreys, and A. P. Sutton, "Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+ U study," *Physical Review B*, vol. 57, no. 3, p. 1505, 1998.
- [126] H. Yuan *et al.*, "A novel BiVO₄/DLC heterojunction for efficient photoelectrochemical water splitting," *Chemical Engineering Journal*, vol. 459, pp. 141637-141637, 2023/3// 2023.
- [127] W. Zhao *et al.*, "A novel Z-scheme Ag₃VO₄/BiVO₄ heterojunction photocatalyst: Study on the excellent photocatalytic performance and photocatalytic mechanism," *Applied Catalysis B: Environmental*, vol. 245, pp. 448-458, 2019/5// 2019.
- [128] G. Malmros, "The crystal structure of α-Bi₂O₃," *Acta Chem. Scand*, vol. 24, no. 2, p. 384, 1970.
- [129] Z. Wu, Z. Zou, J. Huang, and F. Gao, "NiFe₂O₄ nanoparticles/NiFe layered double-hydroxide nanosheet heterostructure array for efficient overall water splitting at large current densities," *ACS applied materials & interfaces*, vol. 10, no. 31, pp. 26283-26292, 2018.

- [130] X. Cai, X. Shen, L. Ma, Z. Ji, C. Xu, and A. Yuan, "Solvothermal synthesis of NiCo-layered double hydroxide nanosheets decorated on RGO sheets for high performance supercapacitor," *Chemical Engineering Journal*, vol. 268, pp. 251-259, 2015/5// 2015.
- [131] S. Liu *et al.*, "Promoting the hydrogen evolution reaction through oxygen vacancies and phase transformation engineering on layered double hydroxide nanosheets," *Journal of Materials Chemistry A*, vol. 8, no. 5, pp. 2490-2497, 2020.
- [132] X. Liu, W. Que, Y. Xing, Y. Yang, X. Yin, and J. Shao, "New architecture of a petal-shaped Nb₂O₅ nanosheet film on FTO glass for high photocatalytic activity," *RSC advances*, vol. 6, no. 12, pp. 9581-9588, 2016.
- [133] A. Adjimi, M. L. Zeggar, N. Attaf, and M. S. Aida, "Fluorine-doped tin oxide thin films deposition by sol-gel technique," *Journal of Crystallization Process and Technology*, vol. 8, no. 04, p. 89, 2018.
- [134] G. Zhang and X. W. Lou, "General solution growth of mesoporous NiCo₂O₄ nanosheets on various conductive substrates as high-performance electrodes for supercapacitors," *Advanced materials*, vol. 25, no. 7, pp. 976-979, 2013.
- [135] K. M. AlAqad, T. A. Kandiel, and C. Basheer, "Synergy between in-situ immobilized MoS₂ nanosheets and TiO₂ nanotubes for efficient electrocatalytic hydrogen evolution," *International Journal of Hydrogen Energy*, vol. 47, no. 4, pp. 2366-2377, 2022.
- [136] M. Shao, F. Ning, M. Wei, D. G. Evans, and X. Duan, "Hierarchical nanowire arrays based on ZnO core-layered double hydroxide shell for largely enhanced photoelectrochemical water splitting," *Advanced Functional Materials*, vol. 24, no. 5, pp. 580-586, 2014.
- [137] Y. Tang, R. Wang, Y. Yang, D. Yan, and X. Xiang, "Highly enhanced photoelectrochemical water oxidation efficiency based on triadic quantum dot/layered double hydroxide/BiVO₄ photoanodes," *ACS applied materials & interfaces*, vol. 8, no. 30, pp. 19446-19455, 2016.
- [138] H. She, P. Yue, X. Ma, J. Huang, L. Wang, and Q. Wang, "Fabrication of BiVO₄ photoanode cocatalyzed with NiCo-layered double hydroxide for enhanced photoactivity of water oxidation," *Applied Catalysis B: Environmental*, vol. 263, p. 118280, 2020.
- [139] R. Ramachandran, Y. Lan, Z.-X. Xu, and F. Wang, "Construction of NiCo-Layered Double Hydroxide Microspheres from Ni-MOFs for High-Performance Asymmetric Supercapacitors," *ACS Applied Energy Materials*, vol. 3, no. 7, pp. 6633-6643, 2020/7// 2020.
- [140] Z. Cai *et al.*, "Introducing Fe²⁺ into nickel-iron layered double hydroxide: local structure modulated water oxidation activity," *Angewandte Chemie*, vol. 130, no. 30, pp. 9536-9540, 2018.
- [141] Y. Yang *et al.*, "Highly active trimetallic NiFeCr layered double hydroxide electrocatalysts for oxygen evolution reaction," *Advanced Energy Materials*, vol. 8, no. 15, p. 1703189, 2018.
- [142] C. Zachäus, F. F. Abdi, L. M. Peter, and R. Van De Krol, "Photocurrent of BiVO₄ is limited by surface recombination, not surface catalysis," *Chemical science*, vol. 8, no. 5, pp. 3712-3719, 2017.

- [143] V. Nair, C. L. Perkins, Q. Lin, and M. Law, "Textured nanoporous Mo:BiVO₄ photoanodes with high charge transport and charge transfer quantum efficiencies for oxygen evolution," *Energy & Environmental Science*, vol. 9, no. 4, pp. 1412-1429, 2016.
- [144] L. Gao *et al.*, "Dual Modification of a BiVO₄ Photoanode for Enhanced Photoelectrochemical Performance," *ChemSusChem*, vol. 11, no. 15, pp. 2502-2509, 2018/8// 2018.
- [145] T. W. Kim, Y. Ping, G. A. Galli, and K.-S. Choi, "Simultaneous enhancements in photon absorption and charge transport of bismuth vanadate photoanodes for solar water splitting," *Nature communications*, vol. 6, no. 1, p. 8769, 2015.
- [146] Y. Wang *et al.*, "Charge relays via dual carbon-actions on nanostructured BiVO₄ for high performance photoelectrochemical water splitting," *Advanced Functional Materials*, vol. 32, no. 13, p. 2112738, 2022.
- [147] Y. He *et al.*, "Surface reformation of 2D MXene by in situ LaF₃-decorated and enhancement of energy storage in lithium-ion batteries," *Journal of Materials Science: Materials in Electronics*, vol. 31, pp. 6735-6743, 2020.
- [148] A. C. Khot, T. D. Dongale, J. H. Park, A. V. Kesavan, and T. G. Kim, "Ti₃C₂-based MXene oxide nanosheets for resistive memory and synaptic learning applications," *ACS Applied Materials & Interfaces*, vol. 13, no. 4, pp. 5216-5227, 2021.
- [149] L.-X. Liu, J. Fu, L.-P. Jiang, J.-R. Zhang, W. Zhu, and Y. Lin, "Highly efficient photoelectrochemical reduction of CO₂ at low applied voltage using 3D Co-Pi/BiVO₄/SnO₂ nanosheet array photoanodes," *ACS Applied Materials & Interfaces*, vol. 11, no. 29, pp. 26024-26031, 2019.
- [150] R. L. Frost, D. A. Henry, M. L. Weier, and W. Martens, "Raman spectroscopy of three polymorphs of BiVO₄: clinobisvanite, dreyerite and pucherite, with comparisons to (VO₄)₃-bearing minerals: namibite, pottsite and schumacherite," *Journal of Raman Spectroscopy: An International Journal for Original Work in all Aspects of Raman Spectroscopy, Including Higher Order Processes, and also Brillouin and Rayleigh Scattering*, vol. 37, no. 7, pp. 722-732, 2006.
- [151] J. Zhang, Y. Huang, X. Lu, J. Yang, and Y. Tong, "Enhanced BiVO₄ photoanode photoelectrochemical performance via borate treatment and a NiFeOx cocatalyst," *ACS Sustainable Chemistry & Engineering*, vol. 9, no. 24, pp. 8306-8314, 2021.
- [152] A. Sarycheva and Y. Gogotsi, "Raman spectroscopy analysis of the structure and surface chemistry of Ti₃C₂T_x MXene," *Chemistry of Materials*, vol. 32, no. 8, pp. 3480-3488, 2020.
- [153] H. Ghassemi *et al.*, "In situ environmental transmission electron microscopy study of oxidation of two-dimensional Ti₃C₂ and formation of carbon-supported TiO₂," *Journal of Materials Chemistry A*, vol. 2, no. 35, pp. 14339-14343, 2014.
- [154] Z. Wen, T. Meng, J. Haimiao, J. Haiying, and T. Junwang, "Highly matched BiVO₄/WO₃ nanobowl heterojunction photoanode for efficient photoelectrochemical water splitting," *Journal of Catalysis*, vol. 43, no. 9, p. 2321, 2022.
- [155] S. Zhang *et al.*, "Ultrafine Sb pillared few-layered Ti₃C₂T_x MXenes for advanced sodium storage," *ACS Applied Energy Materials*, vol. 4, no. 9, pp. 9806-9815, 2021.

- [156] R. Zheng *et al.*, "In situ fabricating oxygen vacancy-rich TiO₂ nanoparticles via utilizing thermodynamically metastable Ti atoms on Ti₃C₂T_x MXene nanosheet surface to boost electrocatalytic activity for high-performance Li–O₂ batteries," *ACS applied materials & interfaces*, vol. 11, no. 50, pp. 46696-46704, 2019.
- [157] T. Katsuki, Z. N. Zahran, Y. Tsubonouchi, D. Chandra, N. Hoshino, and M. Yagi, "p–n junction formation between CoPi and α -Fe₂O₃ layers enhanced photo-charge separation and catalytic efficiencies for efficient visible-light-driven water oxidation," *Sustainable Energy & Fuels*, vol. 7, no. 12, pp. 2910-2922, 2023.
- [158] A. Zaban, M. Greenshtein, and J. Bisquert, "Determination of the electron lifetime in nanocrystalline dye solar cells by open-circuit voltage decay measurements," *ChemPhysChem*, vol. 4, no. 8, pp. 859-864, 2003.
- [159] S. Hernández, G. Gerardi, K. Bejtko, A. Fina, and N. Russo, "Evaluation of the charge transfer kinetics of spin-coated BiVO₄ thin films for sun-driven water photoelectrolysis," *Applied Catalysis B: Environmental*, vol. 190, pp. 66-74, 2016/8// 2016.
- [160] D. Cardenas-Morcoso, A. Bou, S. Ravishankar, M. García-Tecedor, S. Gimenez, and J. Bisquert, "Intensity-modulated photocurrent spectroscopy for solar energy conversion devices: What does a negative value mean?," *ACS Energy Letters*, vol. 5, no. 1, pp. 187-191, 2019.
- [161] X. Xu *et al.*, "High-yield Ti₃C₂T_x MXene–MoS₂ integrated circuits," *Advanced Materials*, vol. 34, no. 48, p. 2107370, 2022.
- [162] V.-I. Merupo, S. Velumani, K. Ordon, N. Errien, J. Szade, and A.-H. Kassiba, "Structural and optical characterization of ball-milled copper-doped bismuth vanadium oxide (BiVO₄)," *CrystEngComm*, vol. 17, no. 17, pp. 3366-3375, 2015.
- [163] J. Peña, P. Bouvier, M. Hneda, C. Goujon, and O. Isnard, "Raman spectra of vanadates MV₂O₆ (M= Mn, Co, Ni, Zn) crystallized in the non-usual columbite-type structure," *Journal of Physics and Chemistry of Solids*, vol. 154, p. 110034, 2021.
- [164] N. Khanehsari, M. Amjadi, T. Hallaj, and V. Shafiei-Irannejad, "NiV₂O₆ nanoflowers as an oxidase-mimic nanozyme for sensitive fluorimetric assay of glutathione," *Microchemical Journal*, p. 110160, 2024.
- [165] C. Balamurugan *et al.*, "Hydrothermally Grown Dual-Phase Heterogeneous Electrocatalysts for Highly Efficient Rechargeable Metal-Air Batteries with Long-Term Stability," *Advanced Science*, vol. 9, no. 32, p. 2203663, 2022.
- [166] J. Su, T. Zhang, and L. Wang, "Engineered WO nanorods for conformal growth of WO/BiVO₄ core-shell heterojunction towards efficient photoelectrochemical water oxidation," *Journal of Materials Science: Materials in Electronics*, vol. 28, no. 5, 2017.
- [167] N. Iqbal, I. Khan, Z. H. A. Yamani, and A. Qurashi, "A facile one-step strategy for in-situ fabrication of WO₃-BiVO₄ nanoarrays for solar-driven photoelectrochemical water splitting applications," *Solar Energy*, vol. 144, pp. 604-611, 2017.
- [168] Z. Zhang, M. Wang, W. Cui, and H. Sui, "Synthesis and characterization of a core-shell BiV₄@gC₃N₄ photo-catalyst with enhanced photocatalytic activity under visible light irradiation," *RSC Advances*, vol. 7, no. 14, pp. 8167-8177, 2017.

- [169] Y. Li, H. Sun, Y. Yang, Y. Cao, W. Zhou, and H. Chai, "Controllable fabrication of NiV_2O_6 nanosphere as a high-performance flexible all-solid-state electrode material for supercapacitors," *Journal of Colloid and Interface Science*, vol. 580, pp. 298-307, 2020.
- [170] T. Palaniselvam *et al.*, "Vastly enhanced BiVO_4 photocatalytic OER performance by NiCoO_2 as cocatalyst," *Advanced Materials Interfaces*, vol. 4, no. 19, p. 1700540, 2017.
- [171] Z. Zhang, X. Huang, B. Zhang, and Y. Bi, "High-performance and stable BiVO_4 photoanodes for solar water splitting via phosphorus–oxygen bonded FeNi catalysts," *Energy & Environmental Science*, vol. 15, no. 7, pp. 2867-2873, 2022.
- [172] Z. Chen *et al.*, "Photoelectrochemical Water Splitting: Standards, Experimental Methods, and Protocols," in *Photoelectrochemical Water Splitting*(SpringerBriefs in Energy: Springer New York, 2013, pp. 7-16.
- [173] H. W. Jeong, T. H. Jeon, J. S. Jang, W. Choi, and H. Park, "Strategic Modification of BiVO_4 for Improving Photoelectrochemical Water Oxidation Performance," *The Journal of Physical Chemistry C*, vol. 117, no. 18, pp. 9104-9112, 2013/05/09 2013.
- [174] B. Klahr, S. Gimenez, F. Fabregat-Santiago, J. Bisquert, and T. W. Hamann, "Photoelectrochemical and impedance spectroscopic investigation of water oxidation with “Co-Pi”-coated hematite electrodes," *Journal of the American chemical society*, vol. 134, no. 40, pp. 16693-16700, 2012.
- [175] K. Fuku and K. Sayama, "Efficient oxidative hydrogen peroxide production and accumulation in photoelectrochemical water splitting using a tungsten trioxide/bismuth vanadate photoanode," *Chemical communications*, vol. 52, no. 31, pp. 5406-5409, 2016.
- [176] R. Sánchez-Albores *et al.*, "Characterization and photoelectrochemical evaluation of BiVO_4 films developed by thermal oxidation of metallic Bi films electrodeposited," *Materials Science in Semiconductor Processing*, vol. 153, p. 107184, 2023.
- [177] F. Le Formal, K. Sivula, and M. Grätzel, "The transient photocurrent and photovoltage behavior of a hematite photoanode under working conditions and the influence of surface treatments," *The Journal of Physical Chemistry C*, vol. 116, no. 51, pp. 26707-26720, 2012.
- [178] I. Y. Ahmet *et al.*, "Planar and Nanostructured n-Si/Metal-Oxide/ $\text{WO}_3/\text{BiVO}_4$ Monolithic Tandem Devices for Unassisted Solar Water Splitting," *Advanced Energy and Sustainability Research*, vol. 1, no. 2, p. 2000037, 2020.
- [179] B. H. Meekins and P. V. Kamat, "Got TiO_2 nanotubes? Lithium ion intercalation can boost their photoelectrochemical performance," *ACS nano*, vol. 3, no. 11, pp. 3437-3446, 2009.
- [180] Q. Meng *et al.*, "Remarkable synergy of borate and interfacial hole transporter on BiVO_4 photoanodes for photoelectrochemical water oxidation," *Materials Advances*, vol. 2, no. 13, pp. 4323-4332, 2021.
- [181] F. Li *et al.*, "A cobalt@cucurbit [5] uril complex as a highly efficient supramolecular catalyst for electrochemical and photoelectrochemical water splitting," *Angewandte Chemie*, vol. 133, no. 4, pp. 2004-2013, 2021.

- [182] F. Li *et al.*, "Electroless plating of NiFeP alloy on the surface of silicon photoanode for efficient photoelectrochemical water oxidation," *ACS applied materials & interfaces*, vol. 12, no. 10, pp. 11479-11488, 2020.
- [183] A. Z. Khan, T. N. Jahangir, T. A. Kandiel, K. Alhooshani, and A. A. Al-Saadi, "Improving charge transfer in phosphate ion-modified hematite photoanode via decoration with gold nanostructures," *Applied Catalysis A: General*, vol. 650, p. 118979, 2023.
- [184] L. Peter, E. Ponomarev, and D. Fermin, "Intensity-modulated photocurrent spectroscopy: reconciliation of phenomenological analysis with multistep electron transfer mechanisms," *Journal of Electroanalytical Chemistry*, vol. 427, no. 1-2, pp. 79-96, 1997.
- [185] A. Walsh, Y. Yan, M. N. Huda, M. M. Al-Jassim, and S.-H. Wei, "Band edge electronic structure of BiVO₄: elucidating the role of the Bi s and V d orbitals," *Chemistry of Materials*, vol. 21, no. 3, pp. 547-551, 2009.
- [186] A. Sleight, H.-Y. Chen, A. Ferretti, and D. Cox, "Crystal growth and structure of BiVO₄," *Materials Research Bulletin*, vol. 14, no. 12, pp. 1571-1581, 1979.
- [187] K. Sayama *et al.*, "Photoelectrochemical decomposition of water into H₂ and O₂ on porous BiVO₄ thin-film electrodes under visible light and significant effect of Ag ion treatment," *The Journal of Physical Chemistry B*, vol. 110, no. 23, pp. 11352-11360, 2006.
- [188] H. Luo, A. H. Mueller, T. M. McCleskey, A. K. Burrell, E. Bauer, and Q. Jia, "Structural and photoelectrochemical properties of BiVO₄ thin films," *The Journal of Physical Chemistry C*, vol. 112, no. 15, pp. 6099-6102, 2008.
- [189] A. Le Bail and M.-A. Lafontaine, "Structure determination of NiV₂O₆ from X-ray powder diffraction: a rutile-ramsdellite intergrowth," *European journal of solid state and inorganic chemistry*, vol. 27, no. 5, pp. 671-680, 1990.
- [190] H. X. Dang, A. J. Rettie, and C. B. Mullins, "Visible-light-active NiV₂O₆ films for photoelectrochemical water oxidation," *The Journal of Physical Chemistry C*, vol. 119, no. 26, pp. 14524-14531, 2015.
- [191] Z. Cao, M. Harb, S. Lardhi, and L. Cavallo, "Impact of interfacial defects on the properties of monolayer transition metal dichalcogenide lateral heterojunctions," *The Journal of Physical Chemistry Letters*, vol. 8, no. 7, pp. 1664-1669, 2017.
- [192] E. Buchaca-Domingo *et al.*, "Direct correlation of charge transfer absorption with molecular donor: acceptor interfacial area via photothermal deflection spectroscopy," *Journal of the American Chemical Society*, vol. 137, no. 16, pp. 5256-5259, 2015.
- [193] D. Eisenberg, H. S. Ahn, and A. J. Bard, "Enhanced Photoelectrochemical Water Oxidation on Bismuth Vanadate by Electrodeposition of Amorphous Titanium Dioxide," *Journal of the American Chemical Society*, vol. 136, no. 40, pp. 14011-14014, 2014/10/08 2014.
- [194] Y. Kanigaridou *et al.*, "Solar photocatalytic degradation of bisphenol A with CuO_x/BiVO₄: Insights into the unexpectedly favorable effect of bicarbonates," *Chemical Engineering Journal*, vol. 318, pp. 39-49, 2017.
- [195] H. Liang *et al.*, "Fast potassium storage in porous CoV₂O₆ nanosphere@ graphene oxide towards high-performance potassium-ion capacitors," *Energy Storage Materials*, vol. 40, pp. 250-258, 2021.

- [196] H. Sun *et al.*, "Largely Improved Cycling Stability of CoV_2O_6 Supercapacitor Electrode Synthesized by Deep Eutectic Solvent," *Journal of Alloys and Compounds*, p. 174555, 2024.
- [197] D. Zhou, L.-X. Pang, J. Guo, H. Wang, X. Yao, and C. Randall, "Phase Evolution, Phase Transition, Raman Spectra, Infrared Spectra, and Microwave Dielectric Properties of Low Temperature Firing $(\text{K}_{0.5x}\text{Bi}_{1-0.5x})(\text{Mo}_x\text{V}_{1-x})\text{O}_4$ Ceramics with Scheelite Related Structure," *Inorganic Chemistry*, vol. 50, no. 24, pp. 12733-12738, 2011.
- [198] Q. Yan *et al.*, "Solar fuels photoanode materials discovery by integrating high-throughput theory and experiment," *Proceedings of the National Academy of Sciences*, vol. 114, no. 12, pp. 3040-3043, 2017.
- [199] P. Varma and D. A. Reddy, "Promoting the BiVO_4 Photoanode Solar Water Oxidation Performance by Coating Hole-Blocking and Oxygen Evolution Layers," *Energy & Fuels*, vol. 37, no. 10, pp. 7401-7410, 2023.
- [200] X. He *et al.*, "A facile method to synthesize CoV_2O_6 as a high-performance supercapacitor cathode," *RSC advances*, vol. 9, no. 17, pp. 9475-9479, 2019.
- [201] R. Narayanan, A. Dewan, and D. Chakraborty, "Complimentary effects of annealing temperature on optimal tuning of functionalized carbon- V_2O_5 hybrid nanobelts for targeted dual applications in electrochromic and supercapacitor devices," *RSC advances*, vol. 8, no. 16, pp. 8596-8606, 2018.
- [202] S. Wang, P. Chen, J. H. Yun, Y. Hu, and L. Wang, "An electrochemically treated BiVO_4 photoanode for efficient photoelectrochemical water splitting," *Angewandte Chemie International Edition*, vol. 56, no. 29, pp. 8500-8504, 2017.
- [203] R. Peat and L. Peter, "A study of the passive film on iron by intensity modulated photocurrent spectroscopy," *Journal of electroanalytical chemistry and interfacial electrochemistry*, vol. 228, no. 1-2, pp. 351-364, 1987.
- [204] C. Zachäus, F. F. Abdi, L. M. Peter, and R. Van De Krol, "Photocurrent of BiVO_4 is limited by surface recombination, not surface catalysis," *Chemical Science*, vol. 8, no. 5, pp. 3712-3719, 2017/5// 2017.

Vitae

Name	:TAHIR NAVEED JAHANGIR
Nationality	:Pakistani
Date of Birth	:12/9/1985
Contact Number	:+92-306-5393581
Email	:tahirnaveedjahangir@mail.com
Address	:Tahir Naveed Jahangir, Taqwa Colony Ward No. & Jhang City, Dist. Jhang, 35200, Pakistan
Academic Background	: M. Phil. in Chemistry, (2013) University of Agriculture, Faisalabad, Pakistan. M. Sc in Chemistry (16 years education) (2009) GC University, Faisalabad, Pakistan.
Publications	1. Jahangir, T. N.; Abdel-Azeim, S.; Kandiel, T. A.; BiVO₄ Photoanode with NiV₂O₆ Back Contact Interfacial Layer for Improved Hole-Diffusion Length and Photoelectrochemical Water Oxidation Activity, ACS: Applied Materials and Interfaces, (2024) DOI: 10.1021/acsami.4c05489 2. Jahangir, T. N.; Kandiel, T. A. Mahar. N; Khan, A. Z.; Saadi, A. A. A. Exploring the role of Ti₃C₂T_xMXene in photoelectrochemical water splitting over Solution-processed BiVO₄ Photoanode, Elsevier: Materials Today Energy, 101469 (2024) DOI: 10.1016/j.mtener.2023.101469 3. Jahangir, T. N.; Kandiel, T. A.; Fatima, W.; Abdalmawla, A. M.; Ahmed, A. A.; Ahmed, Y.A. Insights into the Role of Co₃O₄/Ti₃C₂ MXene Hybrid Material in Photoelectrochemical Water Oxidation over BiVO₄ Photoanode, Elsevier: Journal of Environmental Chemical Engineering, 113058 (2024) DOI: 10.1016/j.jece.2024.113058 4. Jahangir, T. N.; Khan, A. Z.; Kandiel, T. A.; Ali, B. M. E. Insights into the Charge Transfer Kinetics in BiVO₄ Photoanodes Modified with Transition Metal-Based Oxygen Evolution Electrocatalysts, Elsevier: Catalysis Today, 413-415 (2023) 113918 DOI: 10.1016/j.cattod.2022.09.024 5. Khan, A. Z.; Jahangir, T. N.; Kandiel, T. A.; Abdel-Azeim, S.; Alhooshani, K. Phosphate Ions Interfacial Drift

Layer to Enhance the Performance of CoFe–Prussian blue Hematite Photoanode towards Water Splitting, **Elsevier: Applied Catalysis B: Environmental**, (2022) 121014, DOI: [10.1016/j.apcatb.2021.121014](https://doi.org/10.1016/j.apcatb.2021.121014)

6. Khan, A. Z.; **Jahangir, T. N.**; Kandiel, T. A.; Alhooshani, K. Saadi, A. A. A. Improving Charge Transfer in Phosphate Ion-Modified Hematite Photoanode via Decoration with Gold Nanostructures, **Elsevier: Applied Catalysis A: General**, 650 (2023) 118979 DOI: [10.1016/j.apcata.2022.118979](https://doi.org/10.1016/j.apcata.2022.118979)

7. AlAqad. K. M; Kandiel. T. T.; **Jahangir. T. N.**; Qamar. M.; Chanbasha. B. TiO₂ nanotubes modified with cobalt oxyphosphide spheres for efficient electrocatalytic hydrogen evolution reaction in alkaline medium, **Elsevier: Electrochimica Acta**, 142436 (2023) DOI: [10.1016/j.electacta.2023.142436](https://doi.org/10.1016/j.electacta.2023.142436)