

Synthesis and Characterization of Electrocatalysts based on Boron and Earth-abundant Transition Metals for Electrochemical Water Splitting

by

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Koç University

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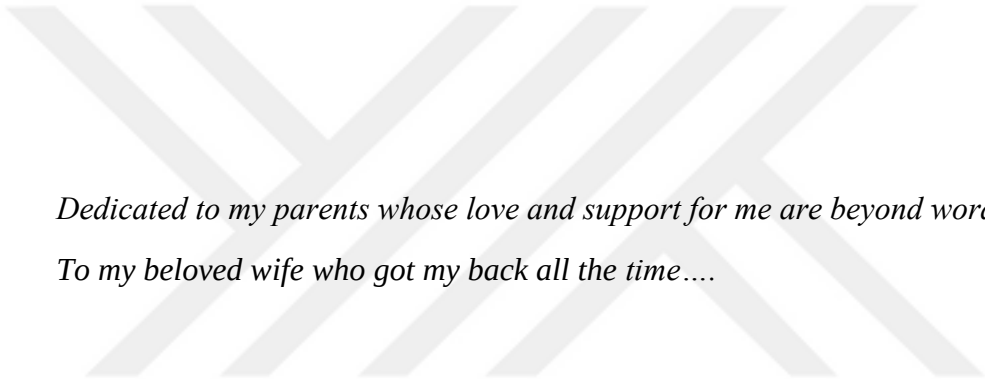
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Dedicated to my parents whose love and support for me are beyond words....

To my beloved wife who got my back all the time....

ABSTRACT

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Ebrahim Sadeghi

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As the world grapples with growing environmental challenges and an ever-expanding population, the need for a sustainable alternative to fossil fuels has become an unprecedented challenge. The quest for sustainable energy production strategies has converged on the electrocatalytic water splitting process integrated with renewable energy resources. The successful realization of this process hinges on the development of competent, cost-effective, and earth-abundant electrocatalysts capable of driving both the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER) efficiently within the same electrolyte.

Over the course of four years of research, this PhD thesis has dedicated extensive efforts to address this challenge by investigating novel electrocatalysts. The following key contributions have been made. **1) Novel Electrocatalysts:** Synthesis, characterization, and electrochemical evaluation of newfangled electrocatalysts with the formal composition of $\text{Mg}_{1-x}\text{TM}_x\text{B}_2$ ($x = 0.025, 0.05, \text{ and } 0.1$; $\text{TM} = \text{Fe and Co}$). The study primarily focuses on their performance in both HER and OER under 1.0 M KOH medium. Among these catalysts, $\text{Mg}_{0.95}\text{Co}_{0.05}\text{B}_2$ has demonstrated exceptional HER performance, boasting an overpotential of 470 mV at 10 mA cm^{-2} . The findings suggest a promising direction in the development of highly competent and low-cost electrocatalysts. **2) Transformative Materials:** Development of electrocatalysts with a formal composition of $\text{V}_{1-x}\text{Co}_x\text{B}_2$ ($x = 0, 0.05, 0.1, \text{ and } 0.2$) for use in the oxygen-evolving reaction. The incorporation of Co into the VB_2 structure has led to a dramatic transformation in morphology, reducing the overpotential to 200 mV at 10 mA cm^{-2} . This performance rivals that of the noble-metal catalyst RuO_2 (290 mV) and demonstrates notable durability under 1.0 M KOH conditions. **3) Metal Organic Frameworks (MOFs):** Exploration of nanocomposites based on NCM [$\text{N} = \text{Ni}, \text{C} = \text{Co}, \text{M} = \text{Fe, Cu, Zn}$]/Ni-BDC@NF, directly developed on nickel foam (NF), revealing unique electronic structure modulation. Notably, the NCF/Ni-BDC catalyst demonstrates outstanding OER performance, requiring only 1.35 V versus a reversible hydrogen electrode (RHE) to achieve 10 mA cm^{-2} current density. This research showcases the potential of 2D MOFs as versatile materials for efficient water splitting. **4) Heterostructures:** Presentation of a high-performance and durable heterostructure of NiMo/CoMoO_4 for the alkaline HER, constructed via a two-pot in situ growth strategy on a NF. The heterostructure exhibits low overpotential (102 mV at 10 mA cm^{-2}) and high Faradaic efficiency. It highlights the synergy of metallic and oxide components, demonstrating superior performance in the HER, a crucial element of water electrolysis for carbon-neutral hydrogen production. **5) MOF-Derived Catalysts:** Introduction of a nanostructured interface between NiMo/CuO@C derived from Cu-MOF, designed and developed on NF, as a competent

HER electrocatalyst in alkaline media. This catalyst shows a low overpotential of 85 mV at 10 mA cm^{-2} , rivalling Pt/C, and exhibits remarkable durability over an extended period of 50 h.

This four-year research endeavor culminates in a comprehensive understanding of advanced electrocatalysts for sustainable water splitting. The thesis underscores the significance of these materials in addressing the global need for clean and efficient hydrogen production, offering a pathway towards a more sustainable and eco-friendly energy future.



ÖZETÇE

Elektrokimyasal Su Ayrıştırma için Bor ve Doğada Bol Bulunan Geçiş Metallerine Dayalı Elektrokatalizörlerin Sentezi ve Karakterizasyonu

Ebrahim Sadeghi

Malzeme Bilimi ve Mühendisliği, Doktora

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Dünya, büyüyen çevresel zorluklarla ve sürekli artan nüfusla başa çıkarken, fosil yakıtlara alternatif sürdürülebilir bir enerji kaynağı sağlamak benzersiz bir zorluk haline gelmiştir. Sürdürülebilir enerji üretim stratejilerinin arayışı, yenilenebilir enerji kaynaklarıyla entegre elektrokatalitik su bölünme sürecinde birleşmiştir. Bu sürecin başarılı bir şekilde gerçekleştirilmesi, aynı elektrolit içinde hem oksijen çıkış reaksiyonu (OER) hem de hidrojen çıkış reaksiyonu (HER) için verimli, maliyet etkili ve yeryüzünde bol bulunan elektrokatalizörlerin geliştirilmesine bağlıdır.

Dört yıl süren bir araştırma süreci boyunca bu doktora tezi, belirtilen zorluğu ele almak için yeni elektrokatalizörleri bulmak için büyük çaba harcamıştır. Şu belirtilen alanlarda ana katkılar sağlanmıştır. **1) Yenilikçi Elektrokatalizörler:** $Mg_{1-x}TM_xB_2$ ($x = 0.025, 0.05, \text{ ve } 0.1$; $TM = Fe \text{ ve } Co$) formal kompozisyonuna sahip yeni elektrokatalizörlerin sentezi, karakterizasyonu ve elektrokimyasal değerlendirmesi. Çalışma, bu katalizörlerin HER ve OER performansına odaklanmış ve $Mg_{0.95}Co_{0.05}B_2$ 'nin 10 mA cm^{-2} akımda 470 mV 'lik aşırı gerilimle olağanüstü HER performansı sergilediğini göstermiştir. Bulgular, yüksek verimli ve düşük maliyetli elektrokatalizörlerin geliştirilmesinde umut verici bir yöne işaret etmektedir. **2) Dönüşümsel Malzemeler:** Oksijen çıkış reaksiyonunda kullanılmak üzere $V_{1-x}Co_xB_2$ ($x = 0, 0.05, 0.1 \text{ ve } 0.2$) formal kompozisyonlu elektrokatalizörlerin geliştirilmesi. Co'nun VB_2 yapısına eklenmesi, morfolojide dramatik bir değişikliğe neden olmuş, 10 mA cm^{-2} 'de 200 mV 'lik aşırı gerilimi azaltmıştır. Bu performans, RuO_2 (290 mV) ile rekabet ederken 1 M KOH koşullarında dikkate değer dayanıklılık göstermiştir. **3) Metal Organik Çerçevesler (MOF'lar):** Nikel köpük üzerine doğrudan geliştirilen NCM/Ni-BDC@NF tabanlı nanokompozitlerin keşfi, benzersiz elektronik yapı modülasyonunu açığa çıkarmıştır. Özellikle NCF/Ni-BDC katalizörü, 10 mA cm^{-2} akım yoğunluğunu elde etmek için bir geri dönüşümlü hidrojen elektroduna karşı yalnızca 1.35 V 'lik aşırı gerilim gerektiren olağanüstü OER performansı sergilemiştir. Bu araştırma, etkili su ayrıştırma için çok yönlü malzemeler olarak 2D MOF'ların potansiyelini sergilemektedir. **4) Heteroyapılar:** Nikel köpük üzerine iki aşamalı yerinde (in situ) büyüme stratejisi ile oluşturulan yüksek performanslı ve dayanıklı bir $NiMo/CoMoO_4$ heteroyapısının oluşturulması. Heteroyapı, 10 mA cm^{-2} 'de 102 mV 'lik aşırı gerilimi ve yüksek Faraday verimliliğini sergilemektedir. Bu, karbon nötral hidrojen üretimi için su elektrolizinin kritik bir unsuru olan HER'de üstün performansın metalik ve oksit bileşiklerin sinerjisi ile elde edilebileceğini vurgulamaktadır. **5) MOF Kökenli Katalizörler:** Alkali ortamda verimli bir HER elektrokatalizörü olarak Cu-MOF'tan türetilmiş $NiMo/CuO@C$ arasında nano yapıda bir arayüzün tasarlanması ve geliştirilmesi. Bu katalizör, 10 mA cm^{-2} 'de 85 mV 'lik aşırı

gerilimiyle Pt/C ile rekabet ederken uzun bir süre boyunca kayda değer dayanıklılık göstermiştir.

Bu dört yıllık araştırma, sürdürülebilir su ayrıştırma reaksiyonları için verimli elektrokatalizörlerin geliştirilmesine odaklanmıştır. Tez, temiz ve verimli hidrojen üretiminin küresel ihtiyaç haline gelişini ve daha sürdürülebilir ve çevre dostu bir enerji geleceğine yol açmak için bu malzemelerin önemini vurgulamaktadır.



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TABLE OF CONTENTS

Chapter 1: An Introduction.....	24
Chapter 2: Hydrogen Energy and Water Splitting.....	26
2.1. Energy Crisis and Alternative Solutions.....	26
2.1.1. Sources of hydrogen	27
2.1.2. Hydrogen production methods.....	28
2.2. Electrocatalytic water splitting for hydrogen production	29
2.2.1. Origin of Electrochemical Activity	31
2.2.2. Hydrogen Evolution Reaction	32
2.2.3. Oxygen Evolution Reaction	33
2.3. Evaluation Criteria	34
2.3.1. Overpotential	35
2.3.2. Tafel Plot	35
2.3.3. Turnover Frequency (TOF).....	36
2.3.4. Faradaic Efficiency.....	37
2.3.5. Stability.....	38
2.4. Electrocatalytic Materials	38
2.4.1. Transition metal borides	38
2.4.2. Synthetic methods.....	40
2.4.3. Transition metal oxides	42
2.4.4. Metal Organic Frameworks (MOFs).....	44
2.4.5. Basic Strategy for Designing of Self Supported MOF	45
Chapter 3: Metal Doped Layered MgB_2 Nanoparticles as Novel Electrocatalysts for Water Splitting.....	50
3.1. Introduction.....	51
3.2. EXPERIMENTAL SECTION	52
3.2.1. Synthesis of Electrocatalysts.....	52
3.2.2. Apparatus and Procedure.....	53

3.3.	RESULTS AND DISCUSSIONS.....	54
3.4.	CONCLUSIONS	68
Chapter 4: Tailoring the morphology of cost-effective vanadium diboride through cobalt substitution for highly efficient alkaline water oxidation		
4.1.	Introduction.....	70
4.2.	EXPERIMENTAL SECTION	71
4.2.1.	Chemical Reagents	71
4.2.2.	Synthesis of Electrocatalysts	71
4.2.3.	Electrode Fabrication	72
4.2.4.	Characterizations	72
4.2.5.	Electrochemical Measurements	72
4.3.	RESULTS AND DISCUSSION	74
4.3.1.	Chemical Studies	74
4.3.2.	Electrochemical Studies	78
4.4.	Investigation of OER Catalytic Mechanism	84
4.5.	CONCLUSIONS	85
Chapter 5: Designing In-situ Grown Ternary Oxide / 2D Ni-BDC MOF Nanocomposites on Nickel Foam as Efficient Electrocatalysts for Electrochemical Water Splitting.....		
5.1.	Introduction.....	87
5.2.	EXPERIMENTAL SECTION	88
5.2.1.	Catalyst Fabrication	88
5.2.2.	Catalyst Characterization	90
5.2.3.	Electrochemical Characterization	91
5.3.	RESULTS AND DISCUSSION	92
5.3.1.	Chemical Studies	92
5.3.2.	Electrocatalytic Activity of the Electrodes for the OER and HER	
	103	
5.3.3.	Post-Electrocatalysis Characterization	113

5.4.	Mechanism Discussion	118
5.5.	CONCLUSIONS	121
Chapter 6: NiMo/CoMoO ₄ heterostructure with confined oxygen vacancy for active and durable alkaline hydrogen evolution reaction		122
6.1.	Introduction.....	123
6.2.	EXPERIMENTAL SECTION	124
6.2.1.	Catalyst Preparation	124
6.2.2.	Materials Characterization	125
6.2.3.	Electrochemical Characterization	126
6.3.	RESULTS AND DISCUSSION	127
6.3.1.	Chemical Studies	127
6.3.2.	Electrochemical Studies	134
6.3.3.	Post- Electrocatalysis Characterization	138
6.4.	Proposed Mechanism	141
6.5.	CONCLUSIONS	143
Chapter 7: In-situ Design of a Nanostructured Interface between NiMo and CuO Derived from Metal–Organic Framework for Enhanced Hydrogen Evolution in Alkaline Solutions		145
7.1.	Introduction.....	146
7.2.	Experimental Section.....	147
7.2.1.	Catalyst Preparation	147
7.2.2.	Electrochemical Characteristics	150
7.3.	RESULTS AND DISCUSSION	151
7.3.1.	Structural Studies	151
7.3.2.	Electrocatalytic Studies	156
7.3.3.	Post-electrocatalysis Characterization	161
7.4.	Proposed Mechanism	162
7.5.	CONCLUSIONS	163
Chapter 8: Conclusion		165

Appendix A.....	168
Appendix B.....	177
Appendix C.....	184
Appendix D.....	201
Appendix E	214
Bibliography	224



List of Tables

Table 2. 1. Annual global hydrogen production share by source	27
Table 3. 1. FWHM values and crystallite size for pure $\text{Mg}_{1-x}\text{TM}_x\text{B}_2$ ($x = 0.025, 0.05,$ and 0.1 ; $\text{TM} = \text{Fe}$ and Co).	57
Table 3. 2. Equivalent-circuit element values for EIS data in the 1 M KOH electrolyte.....	65
Table 4. 1. Calculated values of the equivalent circuit elements for the samples...	84
Table A 1. Energy-dispersive X-ray spectroscopy (EDX) analysis of samples before HER and OER.....	169
Table A 2. Lattice parameters (a and c in the space group $P6/mmm$) of samples investigated.	170
Table A 3. Equivalent-circuit element values for EIS data in the 1 M KOH electrolyte.....	174
Table A 4. Energy-dispersive X-ray spectroscopy (EDX) analysis of the best- performing samples after HER and OER.	175
Table B 1. EDS elemental composition of $\text{V}_x\text{Co}_{1-x}\text{B}_2$ ($x = 0, 0.05, 0.1,$ and 0.2) with and without oxygen.....	178
Table B 2. Surface composition from XPS spectra (in atomic percent) of VB_2 and $\text{V}_{1-x}\text{Co}_x\text{B}_2$ powders.....	183
Table C 1. The quantitative results of XRF analysis of ternary mixed oxides.....	186
Table C 2. The OER, HER, and overall water splitting performances of recent reports on MOF-derivative catalysts in terms of overpotential at 10 mA cm^{-2} (η^{10}) and 50 mA cm^{-2} (η^{50}) current densities.....	191
Table C 3. The OER and HER performances of fabricated catalysts in this work in terms of overpotential at 10 mA cm^{-2} (η^{10}) and 50 mA cm^{-2} (η^{50}) current densities, charge transfer coefficient (α) for OER, and exchange current density (j^0) for HER.	193
Table C 4. Estimated values obtained from the EIS simulations by the ZView software.....	194

Table C 5. . ICP-MS analysis on dissolved elements during OER stability for NCF/Ni-BDC and HER stability for NCZ/Ni-BDC.	199
---	-----

Table D 1. The HER performances of recent reports on NiMo-derivative catalysts in terms of overpotential at 10 mA cm ⁻² (η^{10}) current density.	208
--	-----

Table D 2. Fit parameters from the equivalent circuit for NiMo.	209
--	-----

Table D 3. . Fit parameters from the equivalent circuit for CoMoO ₄	210
---	-----

Table D 4. Fit parameters from the equivalent circuit for NiMo/CoMoO ₄	211
--	-----

Table D 5. Further details derived from BET analysis of the samples.	211
---	-----

Table E 1. Fit parameters from the equivalent circuit for as-fabricated electrodes.	220
--	-----

Table E 2. Further details derived from BET analysis of the samples.	222
---	-----

List of Figures

Figure 2. 1. Scheme of water electrolyzers and the possible reaction pathways in basic and acidic solutions. [1].....	30
Figure 2. 2. a) Scheme of conventional water electrolyzers. b) Water splitting reactions under acidic and alkaline conditions. [11].....	31
Figure 2. 3. Schematic representing possible reaction routes for HER on a cathode. [16]	32
Figure 2. 4. Volcano plot for HER on various metals indicating the relation between observed exchange current density and the hydrogen bonding adsorption strength (ΔE_{M-H}). [16].....	33
Figure 2. 5. The OER mechanism for acid (blue line) and alkaline (red line) conditions. The black line indicates that the oxygen evolution involves the formation of a peroxide ($M-OOH$) intermediate (black line) while another route for direct reaction of two adjacent oxo ($M-O$) intermediates (green) to produce oxygen is possible as well. [81-8]	34
Figure 2. 6. Polarization curves for HER (left) and OER (right). The η_c and η_a are the overpotentials for cathode and anode at the same current (j), respectively. [81-8]	35
Figure 2. 7. a) Polarization curves for cathode (red) and anode (blue) electrode. j_0 is the exchange current when $j_a = j_c$. j_{10} is a commonly agreed value for one to report overpotential (η) at this current (assuming the area is 1 cm^2) value. (b) In the η vs. $\log j$ curve, the exchange current density (j_0) could be derived by extrapolating the curve to $\eta = 0$. Slope b is the Tafel slope, where it is usually assumed that the steeper (larger) the slope is, the worse the electrode kinetics will be (slower current increased in the same given potential comparing in the case of b_1 and b_2). [81-8]	36
Figure 2. 8. The crystal structures of twelve metal diborides: (a) MB_2 ($M = \text{Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and Mn}$), (b) WB_2 , (c) ReB_2 , and (d) RuB_2 . The pink balls represent boron atoms, whereas the light blue, blue, bluish violet and green balls represent the corresponding metal atoms. [82].....	40
Figure 2. 9. Schematic diagram of the growth of Mo_3B layers on Mo foils.] 90[...	42
Figure 2. 10. a,b,c) Different types of bridging ligand utilized for the synthesis of metal organic framework and d,e,f) structure of the corresponding MOFs. [R10]	47
Figure 2. 11. Synthesis of self-supported MOF derived catalysts by hydrothermal method using self-supported MOF-precursor. [R10]	48

Figure 2. 12. Synthesis of self-supported MOF derived catalysts using CVD technique. [R10]	49
Figure 2. 13. Electrochemical transformation of self-supported MOF into metal hydroxide-(oxy)hydroxide nanosheets with applied potential. [R10]	49
Figure 3. 1. Illustration of final states of MgB_2 powder, doped MgB_2 pellets, and the working electrode.	53
Figure 3. 2. XRD patterns of MgB_2 and $\text{Mg}_{1-x}\text{Tm}_x\text{B}_2$ ($x = 0.025, 0.05$, and 0.1 ; $\text{Tm} = \text{Fe}$ and Co): impurity peaks of Mg , MgO , and $\text{FeB/Fe}_2\text{B}$ are marked by *, #, and •, respectively.	56
Figure 3. 3. Schematic design of layered MgB_2 structure. a) along the a-axis, b) along the c-axis.	57
Figure 3. 4. XPS spectra of $\text{Mg } 1s$, $\text{B } 1s$, $\text{O } 1s$, $\text{Co } 2p$, and $\text{Fe } 2p$ in MgB_2 , $\text{Mg}_{0.9}\text{Co}_{0.1}\text{B}_2$, and $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{B}_2$	60
Figure 3. 5. SEM images of a) pure MgB_2 , b) $\text{Mg}_{0.975}\text{Co}_{0.025}\text{B}_2$, c) $\text{Mg}_{0.95}\text{Co}_{0.05}\text{B}_2$, d) $\text{Mg}_{0.9}\text{Co}_{0.1}\text{B}_2$, e) $\text{Mg}_{0.975}\text{Fe}_{0.025}\text{B}_2$, f) $\text{Mg}_{0.95}\text{Fe}_{0.05}\text{B}_2$, and g) $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{B}_2$	61
Figure 3. 6. SEM images of the working electrode surface.	62
Figure 3. 7. Polarization curves of the OER reaction of pure and doped MgB_2	62
Figure 3. 8. Polarization curves of a) the HER reaction of pure and doped MgB_2 , b) and c) Nyquist plots measured at OCP in supporting electrolyte of 1 M KOH.	64
Figure 3. 9. Fundamental electrochemical properties for HER. a) Overpotential at -10 mA cm^{-2} of metal-doped MgB_2 , b) The corresponding Tafel plots of undoped and doped MgB_2 . The colors indicating the same samples pictured in Figure 3. 8.	67
Figure 4. 1. XRD patterns of $\text{V}_{1-x}\text{Co}_x\text{B}_2$ ($x = 0, 0.05, 0.1$, and 0.2).	74
Figure 4. 2. SEM images and corresponding EDS elemental mapping of a) VB_2 and b) $\text{V}_{0.9}\text{Co}_{0.1}\text{B}_2$	76
Figure 4. 3. SEM images of a) VB_2 , b) $\text{V}_{0.95}\text{Co}_{0.05}\text{B}_2$, c) $\text{V}_{0.9}\text{Co}_{0.1}\text{B}_2$, and d) $\text{V}_{0.8}\text{Co}_{0.2}\text{B}_2$	77
Figure 4. 4. a) TEM image of $\text{V}_{0.9}\text{Co}_{0.1}\text{B}_2$, b) Crystal structure of VB_2 , and c) SAED pattern of $\text{V}_{0.9}\text{Co}_{0.1}\text{B}_2$	78
Figure 4. 5. High-resolution XPS spectrum of a) $\text{V } 2p$, b) $\text{B } 1s$, c) $\text{Co } 2p$, and d) $\text{O } 1s$ for $\text{V}_{0.9}\text{Co}_{0.1}\text{B}_2$	79

Figure 4. 6. Electrochemical studies of $V_{1-x}Co_xB_2$ ($x = 0, 0.05, 0.1$, and 0.2) at a scan rate of 5 mV s^{-1} in 1 M KOH a) Polarization curves, b) Tafel plots, c) OER for $V_{0.9}Co_{0.1}B_2$ before and after 12 h water oxidation operation, and d) CV experiments for $V_{0.9}Co_{0.1}B_2$ and $V_{0.8}Co_{0.2}B_2$ 81

Figure 4. 7. a) EIS plots and b) Capacitive currents from CV measurements plotted as a function of scan rate..... 82

Figure 4. 8. Faradaic efficiency of the catalyst in 1 M KOH at 1600 rpm under N_2 saturation, a) The disk and ring currents of RRDE plotted as a function of the applied disk potential, and b) The calculated Faradaic efficiency. 85

Figure 5. 1. a) Schematic illustration of nanocomposite catalyst fabrication, NCM/Ni-BDC @NF ($N=Ni$, $C=Co$, $M: F=Fe$, $C=Cu$, and $Z=Zn$, BDC: benzene dicarboxylic acid, NF: Nickel foam), b) Digital photographs of various in-situ grown catalysts on NF with distinctive colors, c, d, e, f, g, h and i) SEM images of Ni-BDC, NCF, NCC, NCZ, NCF/Ni-BDC, NCC/Ni-BDC, and NCZ/Ni-BDC respectively, (inset: low magnification images show the growth of catalyst on NF skeleton)..... 94

Figure 5. 2. Spectroscopic characterizations of selected samples. a) XRD patterns of blank Ni-BDC, NCF/Ni-BDC, NCC/Ni-BDC, and NCZ/Ni-BDC nanocomposites stripped off from NF, b) Shift of XRD (010) peaks for NCF/Ni-BDC, NCC/ Ni-BDC, and NCZ/ Ni-BDC nanocomposites compared to simulated Ni-BDC pattern, c and d) XPS Ni 2p, Co 2p, and Fe 2p spectra for NCF and NCF/Ni-BDC, respectively, e and f) XPS Ni 2p, Co 2p, and Zn 2p spectra for NCZ and NCZ/Ni-BDC, respectively..... 99

Figure 5. 3. Morphological, structural, and microstructural characterizations of the selected sample. a) TEM photographs of blank Ni-BDC with different magnifications (inset: SAED image of Ni-BDC), b and c) TEM and HR-TEM images of NCF/Ni-BDC and NCZ/Ni-BDC, respectively; the first image from left shows the transparent Ni-BDC nanosheet decorated with ternary oxide nanoparticles, third image from left displays the lattice fringes of nanoparticle, white dotted circles show the interfaces and orange dotted lines shows the porosity between nanoparticles, d and e) HAADF-STEM image and the corresponding STEM-EDS mappings of NCF/Ni-BDC and NCZ/Ni-BDC, respectively, and f) AFM image and corresponding height profile of blank Ni-BDC. 102

Figure 5. 4. Electrocatalytic oxygen evolution and hydrogen evolution performances. a and d) OER and HER polarization curves of various catalyst samples: red and blue dotted lines display 10 and 50 mA cm^{-2} , respectively, b and e) OER and HER Tafel plots

obtained by polarization curves, respectively, c and f) Comparison of the overpotential at a current density of 10 mA cm^{-2} and Tafel slope on various OER and HER samples, respectively, g) EIS spectra recorded at 0 V vs RHE, h) Capacitive current density vs scan rate curves for ECSA measurements, i) OER and HER polarization curves before and after long-term durability measurements for best-performing OER (NCF/Ni-BDC) and HER (NCZ/Ni-BDC) samples, and j and k) Long-term durability tests of NCF/Ni-BDC and NCZ/Ni-BDC for OER and HER, respectively at 10, 20, and 50 mA cm^{-2} 111

Figure 5. 5. Post-electrolysis characterizations of NCF/Ni-BDC and NCZ/Ni-BDC after long-term durability tests. a and b) SEM images of post-OER stability NCF/Ni-BDC and post-HER stability NCZ/Ni-BDC, c and e) XRD patterns of NCF/Ni-BDC and NCZ/Ni-BDC before and after stability tests, respectively, d) XPS Ni 2p, Co 2p, and Fe 2p spectra for NCF/Ni-BDC, f) XPS Ni 2p, Co 2p, and Zn 2p spectra for NCZ/Ni-BDC, and g and h) TEM and HR-TEM images of NCF/Ni-BDC and NCZ/Ni-BDC, respectively, and i) Crystal structure transformation after OER stability for NCZ/Ni-BDC sample. 116

Figure 5. 6. Electrocatalytic activity of various electrolyzers for overall water splitting in 1.0 M KOH. a) Schematic and a digital photograph of two-electrode cell used in this work, b) Polarization curves of various catalysts used as the cathode (-) and anode (+) in a two-electrode cell, c) EIS spectra recorded at the cell potential of 0 V for constructed electrolyzers, d) Long-term durability test of the best-performing NCZ/Ni-BDC || NCF/Ni-BDC couple at the constant current density of 20 mA cm^{-2} , e) Electrocatalytic efficiency of overall water splitting for H_2 and O_2 production at $j = 20 \text{ mA cm}^{-2}$ on NCZ/Ni-BDC || NCF/Ni-BDC electrodes, and f) Quantification of the Faraday efficiency of water electrolysis for NCZ/Ni-BDC || NCF/Ni-BDC electrolyzer. 120

Figure 6. 1. a) Schematic illustration of preparation procedure of NiMo/CoMoO₄ heterostructure, b) XRD patterns of NiMo NPs before and after heat treatment at 550 °C under Ar, and c) XRD patterns of pristine β -CoMoO₄ and NiMo/CoMoO₄ (inset: crystal structure of CoMoO₄). 128

Figure 6. 2. Morphological and microstructural characterizations of the samples. SEM images of a) NiMo NPs before heat treatment, b) pristine CoMoO₄, c) NiMo/CoMoO₄ (inset: high magnification SEM images), d) TEM photographs related to pristine CoMoO₄ (inset: SAED pattern), white square showing the high magnification

TEM images of nanorods, green and red squares showing the HR-TEM images of lattice spacing of CoMoO₄, e) TEM photographs related to NiMo/CoMoO₄ (inset: SAED pattern), white square showing the high magnification TEM images of CoMoO₄ nanosheets along with NiMo NPs, green square showing an interface in the heterostructure, red square showing HR-TEM images of NiMo lattice spacing within the heterostructure (irregular enclosed shaped dotted regions show the lattice distortion as a result of oxygen vacancy), and f) HAADF-STEM image and the corresponding EDS–STEM mappings of NiMo/CoMoO₄. 131

Figure 6. 3. Spectroscopic characterizations of the samples. a) From left to right XPS survey of CoMoO₄ and NiMo/CoMoO₄, XPS Co 2p, Mo 3d, and O 1s for CoMoO₄, b) From left to right, XPS Ni 2p, Co 2p, Mo 3d, and O 1s for NiMo/CoMoO₄, c) Raman spectra, d) FT-IR spectra, and e) X-band EPR spectra. 134

Figure 6. 4. Electrocatalytic hydrogen evolution performances in 1.0 M KOH. a) HER polarization curves of the samples, b) 3D bar graphs of overpotentials at 10 and 50 mA cm⁻², c) HER Tafel plots obtained by polarization curves, d) Capacitive current density versus scan rate curves for ECSA measurements, e) EIS spectra recorded at 0 V versus RHE, f) HER Tafel plots derived from EIS experiments, g) TOF (s⁻¹) versus overpotential (mV), and h) Long-term HER durability test of NiMo/CoMoO₄ at an applied current density of 30 mA cm⁻² (inset: HER polarization curves of NiMo/CoMoO₄ before and after long-term HER). 139

Figure 6. 5. Post-electrolysis characterizations of NiMo/CoMoO₄ after long-term HER test. a) SEM image (inset: high magnification SEM image), b) TEM and HR-TEM images (inset: SAED pattern), and c) XPS Ni 2p, Co 2p, Mo 3d, and O 1s spectra. ... 141

Figure 6. 6. a) Schematic presentation of proposed HER mechanism, b) Amount of gas theoretically calculated and experimentally measured for HER using NiMo/CoMoO₄ at 10 mA cm⁻² (inset: homemade electrolysis cell for electrochemical measurements), and c) Quantification of Faradaic efficiency derived from calculated and measured H₂. ... 143

Figure 7. 1. Schematic illustration of preparation procedure of NiMo/Cu-BDC_{Cal}. (CuO derived from Cu-BDC MOF) on NF. 149

Figure 7. 2. Structural and spectroscopic characterizations. a) XRD patterns of Cu-BDC and NiMo/Cu-BDC stripped off from NF, b) XRD patterns of Cu-BDC_{Cal}. and NiMo/Cu-BDC_{Cal}. stripped off from NF, c) Raman spectra for Cu-BDC_{Cal}. and NiMo/Cu-BDC_{Cal}., and d) Ft-IR spectra for Cu-BDC_{Cal}. and NiMo/Cu-BDC_{Cal}.. 152

Figure 7. 3. Morphological and microstructural characterizations. SEM images of a) Cu-BDC, b) NiMo/Cu-BDC, c) Cu-BDC _{Cal.} , d) NiMo/Cu-BDC _{Cal.} , e) STEM, TEM, and HR-TEM images of NiMo/Cu-BDC _{Cal.} (inset: SAED pattern), and f) HAADF-STEM image and the corresponding EDS–STEM mappings of NiMo/Cu-BDC _{Cal.}	155
Figure 7. 4. XPS spectra including survey, Cu 2p, C 1s, O 1s, Ni 2p, and Mo 3d for a) NiMo/Cu-BDC and b) NiMo/Cu-BDC _{Cal.}	158
Figure 7. 5. Electrocatalytic hydrogen evolution performances in 1.0 M KOH. a) HER polarization curves of the samples, b) 3D bar graphs of overpotentials at 10 and 50 mA cm ⁻² , c) HER Tafel plots obtained by polarization curves, d) EIS spectra recorded at –300 mV versus RHE, e) Capacitive current density versus scan rate curves for ECSA measurements, and f) Long-term HER durability test of NiMo/Cu-BDC _{Cal.} at an applied current density of –30 mA cm ⁻² (inset: HER polarization curves of NiMo/Cu-BDC _{Cal.} before and after long-term HER).....	160
Figure 7. 6. Post-electrolysis characterizations of NiMo/Cu-BDC _{Cal.} after long-term HER test. a) SEM image, b) TEM and HR-TEM images, and c) XPS Cu 2p, Ni 2p, and Mo 3d.....	162
Figure 7. 7. Schematic presentation of proposed HER mechanism.	163

Abbreviations

SMR	steam reforming of methane
POX	partial oxidation
EWS	electrocatalytic water splitting
STH	solar to hydrogen
OER	oxygen evolution reaction
HER	hydrogen evolution reaction
PEM	proton exchange membrane
TM	transition metal
TMB	transition metal boride
MDb	metal diboride
TMO	transition metal oxide
TOF	turnover frequency
LSV	linear sweep voltammetry
CV	cyclic voltammetry
RRDE	rotating ring disc electrode
GC	glassy carbon
ORR	oxygen reduction reaction
FE	Faradaic efficiency
CVD	chemical vapor deposition
DFT	density functional theory
MOF	metal organic framework
CUMC	coordinatively unsaturated metal center
NF	nickel foam
MIL	materials institute Lavoisier
ZIF	zeolitic imidazolate framework
PBA	Prussian blue analogue
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
FESEM	field emission scanning electron microscopy
EDX	energy dispersive X-ray spectroscopy
RHE	reversible hydrogen electrode
OCP	open circuit potential

EIS	electrochemical impedance spectroscopy
FWHM	full-width-at-half-maximum
SSA	specific surface area

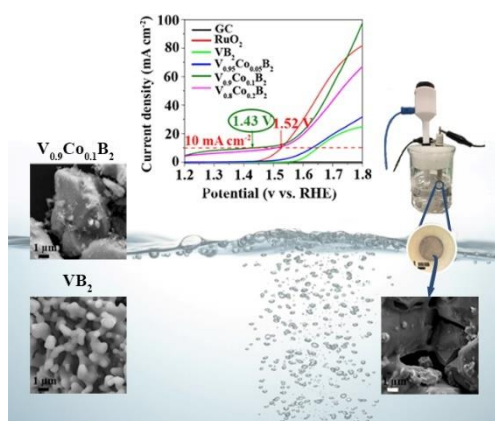
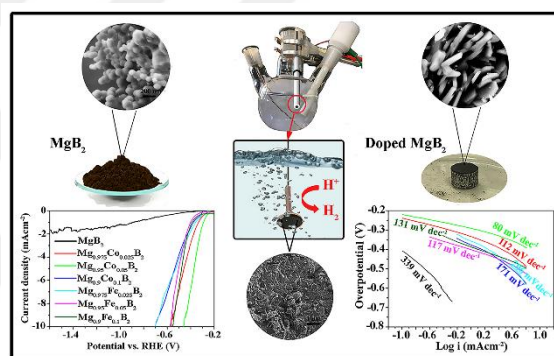


CHAPTER 1

AN INTRODUCTION

The aim of this thesis study is to conduct a detailed investigation of synthesis, materials characterization, and electrochemical properties of transition metal diborides, two-dimensional metal organic frameworks, and transition metal oxides for electrocatalytic water splitting in alkaline media. A comprehensive overview of hydrogen energy, water splitting, two key half-reactions of water splitting, and electrocatalytic materials are presented in **Chapter 2**. The detailed discussions for the specific materials studied during my PhD are included in the following chapters.

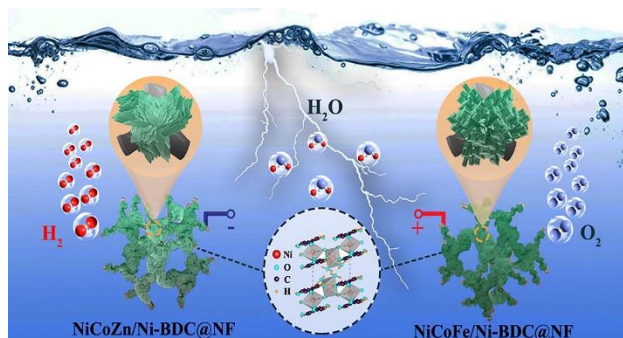
Chapter 3 presents the synthesis, characterization, and electrochemical properties of newfangled electrocatalysts with the formal composition of $\text{Mg}_{1-x}\text{TM}_x\text{B}_2$ ($x = 0.025, 0.05, \text{ and } 0.1$; TM (transition metal) = Fe and Co) primarily in HER as well as OER under 1 M KOH medium. The electrochemical tests revealed that among all the metal-doped MgB_2 catalysts, $\text{Mg}_{0.95}\text{Co}_{0.05}\text{B}_2$ has the best HER performance showing an overpotential of 470 mV at 10 mA cm^{-2} and a Tafel slope of 80 mV dec^{-1} on account of its high purity and fast electron transport.



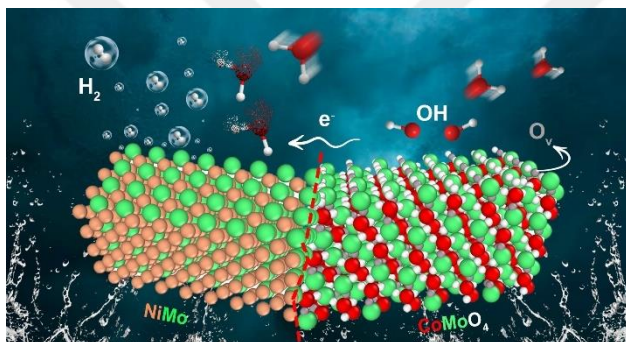
Chapter 4 describes the fabrication of a series of electrocatalysts with a formal composition of $\text{V}_{1-x}\text{Co}_x\text{B}_2$ ($x = 0, 0.05, 0.1, \text{ and } 0.2$) and their application in an oxygen-evolving reaction. The incorporation of Co into the VB_2 structure caused a dramatic transformation in the morphology, resulting in a super low overpotential of 200 mV at 10 mA cm^{-2} for $\text{V}_{0.9}\text{Co}_{0.1}\text{B}_2$ and displaying much greater performance compared to the noble-metal catalyst RuO_2 (290 mV).

Chapter 5 discusses a series of nanocomposites based on NCM/Ni-BDC@NF (N=Ni, C=Co, M: F=Fe, C=Cu, and Z=Zn, BDC: benzene dicarboxylic acid, NF: Nickel foam) were directly developed on NF by a facile yet scalable solvothermal

method. In a two-electrode alkaline electrolyzer, the assembled NCZ/Ni-BDC (cathode) || NCF/Ni-BDC (anode) couple demanded a cell voltage of only 1.58 V to produce 10 mA cm⁻².



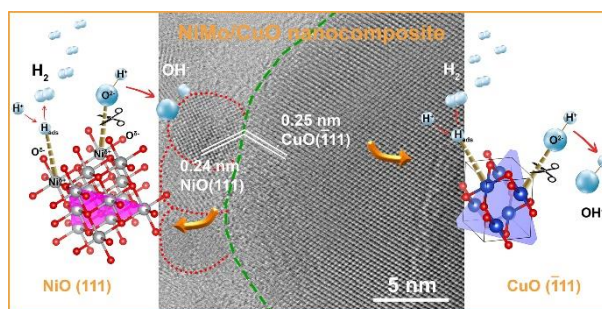
Chapter 6 represents a high-performance and durable heterostructure of



NiMo/CoMoO₄ for the alkaline HER constructed via a two-pot in-situ growth strategy on nickel foam. The heterostructure composed of metallic NiMo and oxygen vacancy (O_v)-confined CoMoO₄ facilitated the H adsorption on the metallic side and

OH adsorption on the oxide side. The hierarchical hybrid catalyst on NF featured a low overpotential of 102 mV at 10 mA cm⁻², approaching the Pt/C (83 mV) in 1.0 M KOH.

Chapter 7 reports a nanostructured interface between NiMo/CuO@C derived from Cu-MOF, designed and developed on nickel foam as a competent HER electrocatalyst in alkaline media. The catalyst exhibited a low overpotential of 85 mV at 10 mA cm⁻² that rivals that of Pt/C (83 mV @ 10 mA cm⁻²).



CHAPTER 2

HYDROGEN ENERGY AND WATER SPLITTING

2.1. Energy Crisis and Alternative Solutions

In the past few years, our planet has grappled with an energy dilemma stemming from resource depletion and a surge in environmental challenges. The predominant utilization of fossil fuels in our existing energy systems is identified as the primary contributor to human-induced carbon dioxide emissions, a significant factor in global warming and climate change.

Furthermore, aside from the diminishing fossil fuel resources and political uncertainties in oil-rich areas, there's an emerging demand for alternative fuels due to stringent emission standards. An effective alternative fuel should meet criteria such as technical viability, economic competitiveness, environmental sustainability, and accessibility. Several potential substitutes have been suggested, encompassing biodiesel, methanol, ethanol, hydrogen, boron, natural gas, liquefied petroleum gas (LPG), Fischer–Tropsch fuel, electricity, and solar fuels.

Among these alternative fuels, hydrogen stands out with the highest specific energy content compared to conventional fuels, and it is also the most abundant element in the universe. Hydrogen is anticipated to significantly contribute to sustainable development, given its potential for virtually unlimited production using renewable energy sources (RES) in the future. The future hydrogen market will be influenced predominantly by four key factors: (1) the prospective cost of hydrogen, (2) the pace of advancements in technologies utilizing hydrogen, (3) potential long-term constraints on greenhouse gases, and (4) the cost of alternative energy systems in competition.

Hydrogen presents itself as a highly promising fuel for the future, offering numerous social, economic, and environmental advantages. It possesses the potential to significantly decrease reliance on foreign oil and mitigate both carbon and criteria emissions in the transportation sector. Only in the past decade has the notion of transitioning to a hydrogen-based economy post-fossil fuels gained widespread attention. Hydrogen bears a notably high energy yield of 122 kJ/g (kilojoules per gram), surpassing hydrocarbon fuels by 2.75 times. Extensive research is being conducted to incorporate

hydrogen into combustion engines and fuel-cell electric vehicles. The global hydrogen market already exceeds \$40 billion annually, encompassing various applications such as ammonia production (49%), petroleum refining (37%), methanol production (8%), and other smaller volume uses (6%).

2.1.1. Sources of hydrogen

All primary sources of energy can be utilized in the process of generating hydrogen. Presently, the primary method for producing hydrogen involves converting natural gas and other lightweight hydrocarbons. In the future, coal and petroleum coke might also be utilized as the raw materials for hydrogen production. As depicted in Table 2. 1, roughly 96% of hydrogen production is derived from the conversion of fossil fuels, such as natural gas reforming. The production of hydrogen from fossil fuels leads to the simultaneous production of carbon dioxide, which is regarded as the primary contributor to the 'greenhouse effect'. These processes rely on non-renewable energy sources for hydrogen production and are not environmentally sustainable. Hence, renewable energy sources and corresponding technologies for hydrogen production will become imperative in the forthcoming decades.

Table 2. 1. Annual global hydrogen production share by source

Source	Bcm ^a /yr	Share (%)
Natural gas	240	48
Oil	150	30
Coal	90	18
Electrolysis	20	4
Total	500	100

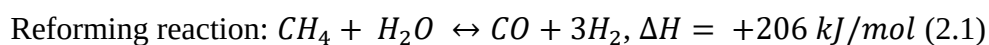
a Bcm: billion cubic meters.

In addition to the above-written sources, hydrogen can also be generated from water through diverse energy sources, including wind, solar, geothermal, hydropower, and nuclear energy. Nuclear energy holds promise for a substantial role in fostering a sustainable hydrogen economy. Utilizing nuclear energy for hydrogen production has the potential to make a noteworthy contribution to meet future hydrogen demands.

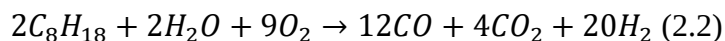
2.1.2. Hydrogen Production Methods

Hydrogen can be produced through various methods, including thermochemical processes, electrochemical processes, photochemical processes, photocatalytic processes, and photo-electrochemical processes. Thermochemical processes for hydrogen production involve chemical reactions aided by heat that result in the release of hydrogen, for example, from hydrocarbons or water. The key advantage of thermochemical processes lies in their higher overall efficiency (thermal to hydrogen), which is approximately 52%, and lower production cost.

Currently, hydrogen is primarily derived from fossil fuels, mainly through steam reforming of methane (SMR) or partial oxidation (POX) of hydrocarbon fuels. Steam reforming of methane is presently the most prevalent technique for hydrogen production from natural gas, constituting nearly 48% of the world's hydrogen production. It is also the most common and cost-effective method for hydrogen production, with an energy consumption rate of approximately 1.23–1.35 GJ-NG/GJ-H₂. The SMR process necessitates high process temperatures, and typically, heat for the process is generated by burning natural gas. When natural gas (or methane from other sources) undergoes steam reformation, it results in a hydrogen-rich gas, usually around 70–75% on a dry basis, with smaller proportions of CH₄ (2–6%), CO (7–10%), and CO₂ (6–14%). SMR involves a three-step process for hydrogen production. Initially, methane is catalytically reformed at elevated temperature and pressure to yield a syngas mixture comprising H₂ and CO. Subsequently, a catalytic shift reaction combines CO and H₂O to generate the H₂ product. The hydrogen product is then purified via adsorption. The reforming step is described by the following reaction:

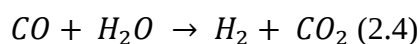
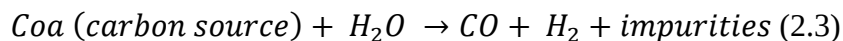


The POX of hydrocarbons involves an exothermic reaction with oxygen and steam. Precise control over the quantities of oxygen and water vapor ensures that the reaction advances without requiring external energy. An illustrative reaction for this procedure is:

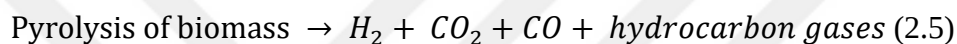


Hydrogen production is also possible through coal gasification, although these methods are less developed compared to the SMR process, they are reasonably established. It's worth noting that hydrogen production from coal constitutes only 18% of global hydrogen production. The primary impediment to its widespread production is the intricate and costly gasification process it entails. The energy consumption for this

process ranges from approximately 1.54 to 1.69 GJ-coal/GJ-H₂. Syngas or artificial water gas (CO + H₂) can be derived from coal and reformed into hydrogen. As coal rank decreases, concentrations of hydrogen and oxygen in coal increase. By carefully adjusting conditions, the water vapor (steam) can be further shifted to produce additional hydrogen through the following reaction:



Hydrogen production can be obtained from biomass through pyrolysis, gasification, steam gasification, steam reforming of bio-oils, and enzymatic decomposition of sugars. Pyrolygneous oils produced from the pyrolysis of lignocellulosic biomass serve as a source for hydrogen production. The primary gaseous products derived from biomass include:



Furthermore, hydrogen can be generated from water or steam through electrolysis, employing less complex technology.[1]

2.2. Electrocatalytic Water Splitting for Hydrogen Production

For over a century, the scientific community has explored the concept of deriving energy from water, dating back to the invention of the voltaic pile. Throughout the years, various methods were devised to separate water molecules and produce hydrogen (H₂), ultimately named as the "fuel of the future". Initially, electrocatalytic water splitting (EWS) stood out as the prominent technological choice, followed by thermal and photocatalytic water decomposition. Among these approaches, photocatalytic water splitting seems to be the most sustainable. However, the industrial implementation of photocatalytic systems remains a distant aspiration mainly due to their inherently low solar to hydrogen (STH) conversion efficiencies. In this context, the significance of electrocatalytic water splitting significantly grows, as it can be integrated with intermittent renewable energy sources (solar, wind, tidal) and offers a practical solution to our energy needs.[2]

Due to its significant energy demands, water electrolysis presently accounts for only 4% of global hydrogen production. Consequently, there's a proactive effort in developing

highly effective electrocatalysts. From both an energy and environmental standpoint, water electrolysis is regarded as a productive and environmentally friendly technology for producing hydrogen and oxygen. This is due to the absence of side reactions that could result in undesirable secondary products. Moreover, generating hydrogen and oxygen through electrolysis using renewable energy sources has the least environmental footprint when compared to alternative methods.[3]

The EWS includes two half-reactions, namely the water oxidation (oxygen evolution reaction, OER) at the anode and the water reduction (hydrogen evolution reaction, HER) at the cathode (Figure 2. 1).[4] To mitigate losses in charge transport during electrochemical processes, conventional water electrolysis typically occurs either in an acidic environment utilizing a proton exchange membrane (PEM) or in an alkaline solution with a diaphragm (depicted in Figure 2. 2a). The specific expressions for the two half-reactions in water splitting can vary depending on the reaction conditions (illustrated in Figure 2. 2b). Under standard conditions, achieving electrochemical water splitting necessitates a thermodynamic potential of 1.23 V (as shown in Figure 2. 2b), equating to an energy input of $\Delta G = 237.1 \text{ kJ mol}^{-1}$. [5]

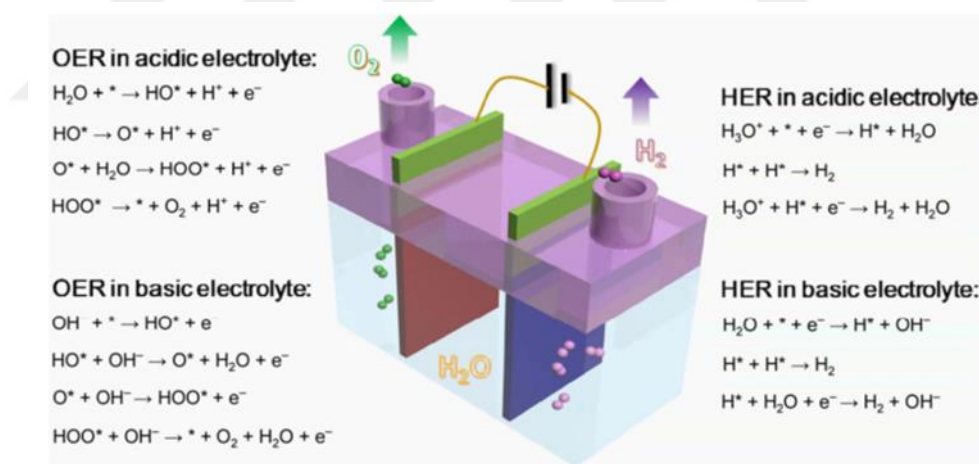


Figure 2. 1. Scheme of water electrolyzers and the possible reaction pathways in basic and acidic solutions.[4]

Regrettably, the slow reaction rates of both the HER and OER necessitate high overpotentials to achieve substantial current density. Consequently, this leads to lower energy conversion efficiencies. As a result, the required input potential for water splitting in practical electrolyzers exceeds the 1.23 V thermodynamic potential. Additionally, electrocatalysts are often essential, such as noble metal-based catalysts like Pt for HER and IrO_2 or RuO_2 for OER in acidic environments, and transition metal (TM)-based catalysts such as Ni electrodes for HER and stainless-steel composites for OER in alkaline

electrolytes. However, the extensive cost, limited availability, and insufficient stability of noble metal-based electrocatalysts, along with the modest activity of noble metal-free electrocatalysts, act as barriers for large-scale H_2 production via water electrolysis.[5]

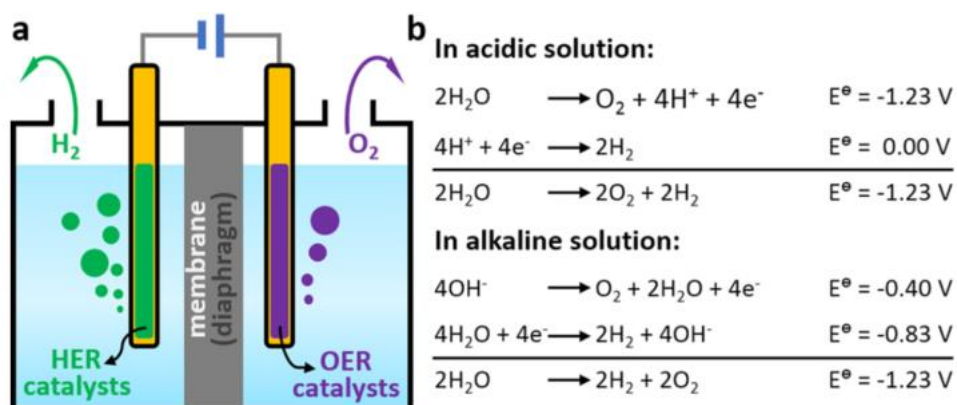
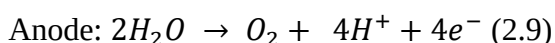
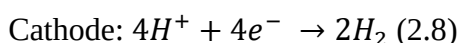


Figure 2. a) Scheme of conventional water electrolyzers. b) Water splitting reactions under acidic and alkaline conditions.[5]

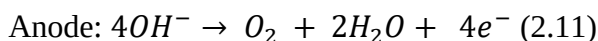
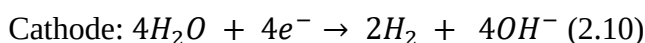
2.2.1. Origin of Electrochemical Activity

The complete mechanism of water splitting involves two nearly simultaneous half-reactions: the HER at the negative electrode and the OER at the positive electrode. Although the process of splitting water molecules into H_2 and O_2 seems straightforward, it unfolds differently in various pH solutions. Equations (2.8–2.13) delineate the half-reactions of water splitting in acidic (Equations (2.8) and (2.9)), basic (Equations (2.10) and (2.11)), and neutral (Equations (2.12) and (2.13)) environments.

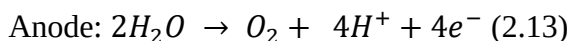
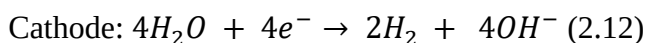
In acidic medium (e.g., hydrochloric acid)



In basic medium (e.g., potassium hydroxide)



In neutral medium (e.g., potassium phosphate buffer)



2.2.2. Hydrogen Evolution Reaction

Among the water splitting half-reactions, HER is relatively simpler, comprising a two-step process:

1. Adsorption of H_2O or H^+ species on the cathode (also known as the Volmer step).
2. Desorption of H_2 from the cathode, occurring via a chemical route (Tafel step) or an electrochemical route (Heyrovsky step) (as illustrated in Figure 2. 3).

For a material to excel as an effective HER catalyst, it should possess specific fundamental characteristics, including a) Abundance of active sites with an optimal electron density, ensuring a balanced bonding strength with the adsorbed H atom (following the Sabatier principle). This facilitates unimpeded adsorption or desorption processes. b) Low charge transfer resistance across the interface and with the underlying electrode material. c) Stability within the electrolyte medium.[2]

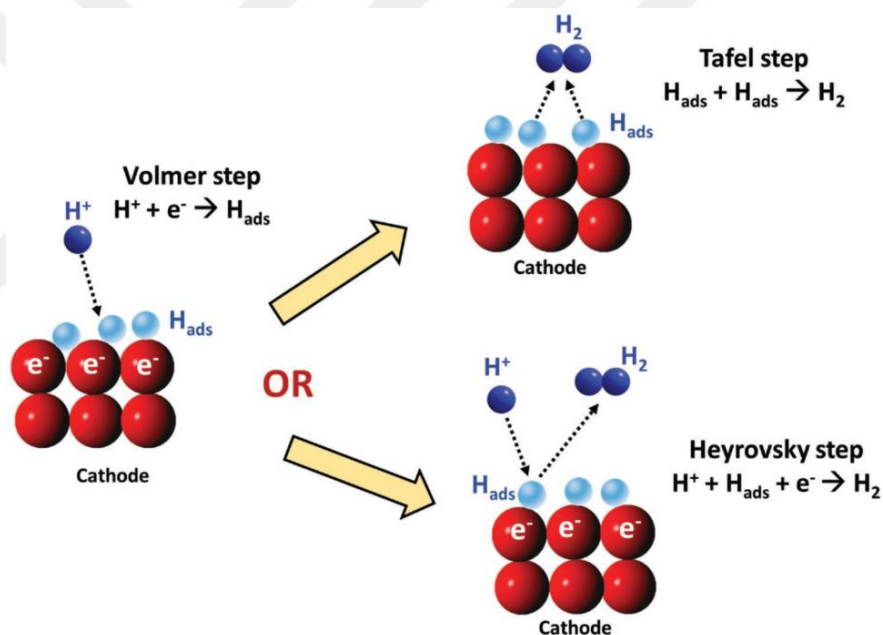


Figure 2. 3. Schematic representing possible reaction routes for HER on a cathode.[2]

These criteria serve as a basis for explaining the performance of various electrocatalysts. For instance, Pt demonstrates exceptionally high HER performance primarily due to its optimal H-bonding strength, positioning it at the peak of the Volcano plot (as shown in Figure 2. 4).

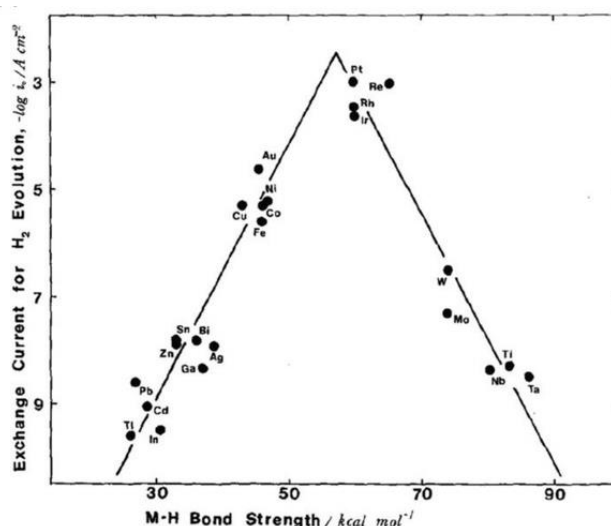
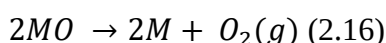
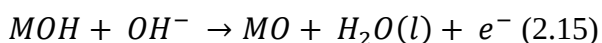


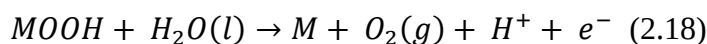
Figure 2. 4. Volcano plot for HER on various metals indicating the relation between observed exchange current density and the hydrogen bonding adsorption strength (ΔE_{M-H}). [2]

2.2.3. Oxygen Evolution Reaction

Numerous research groups have put forth potential mechanisms for the OER occurring at the anode electrode under both acidic (equations (2.14)–(2.18)) and alkaline conditions (equations (2.19)–(2.23)). Within these proposals, there exist both disparities and similarities. Most proposed mechanisms involve common intermediates such as MOH and MO, with the primary divergence revolving around the oxygen-forming reaction. Notably, two distinct approaches are employed to generate oxygen from a MO intermediate, as depicted in Figure 2. 5. One approach, illustrated by the green route in Figure 2. 5, involves the direct combination of 2MO to produce $O_2(g)$ (equation (2.16)). The other approach entails the formation of the MOOH intermediate (equations (2.17) and (2.22)), which subsequently decomposes to $O_2(g)$ (black route in Figure 2. 5; equations (2.18) and (2.23)). Despite this distinction, a consensus prevails that the electrocatalysis of OER is a heterogeneous reaction. The bonding interactions (M–O) within the intermediates (MOH, MO, and MOOH) are widely acknowledged as pivotal for the overall electrocatalytic ability.[6]

Proposed mechanism under acidic conditions





Proposed mechanism under alkaline conditions

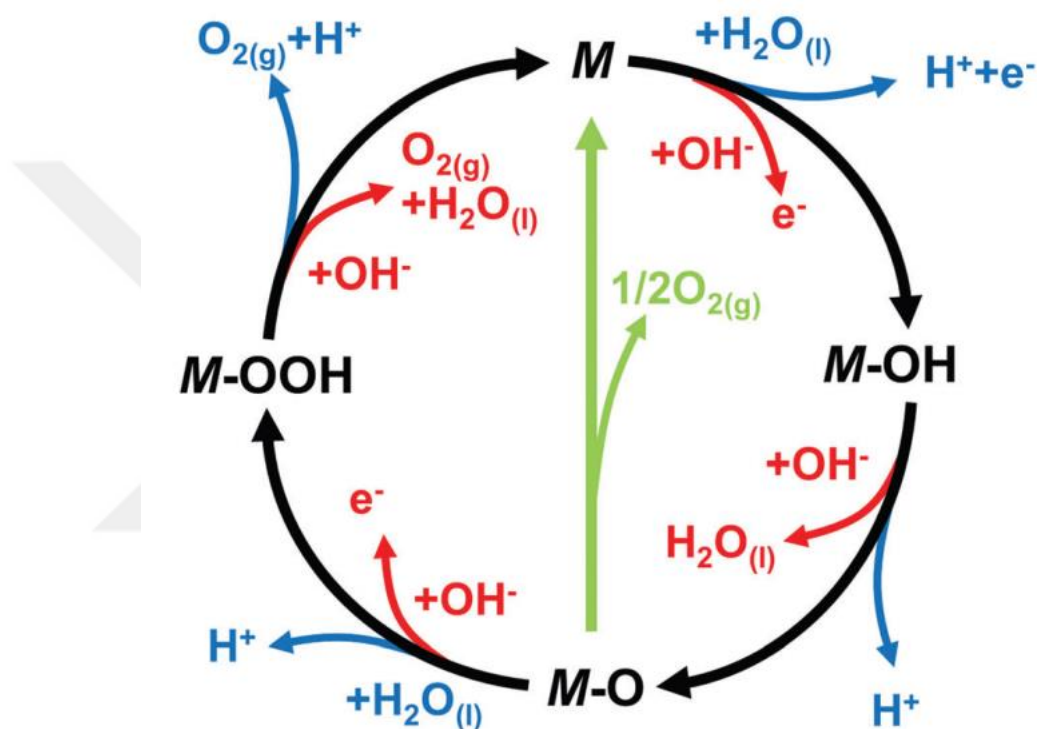
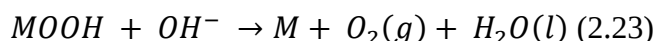
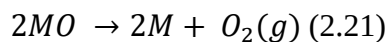
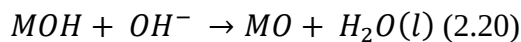
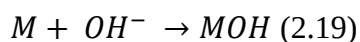


Figure 2. 5. The OER mechanism for acid (blue line) and alkaline (red line) conditions. The black line indicates that the oxygen evolution involves the formation of a peroxide (M–OOH) intermediate (black line) while another route for direct reaction of two adjacent oxo (M–O) intermediates (green) to produce oxygen is possible as well.[6]

2.3.Evaluation Criteria

As discussed earlier, the change in free energy under standard conditions (ΔG°) when converting one mole of water molecules into hydrogen and oxygen gases is +237.2 kJ mol⁻¹. Clearly, this reaction requires an input of energy, indicated by a positive enthalpy change (ΔH°) of +286 kJ mol⁻¹ for the formation of one mole of H₂. Evaluating the efficiency of an electrocatalyst often involves considering the current density at a specific potential. The theoretical electrical potential for a reversible water electrolysis cell is 1.23

V, 0 V for the HER, and 1.23 V for the OER, respectively. Achieving a reasonable reaction rate necessitates an additional potential, termed overpotential (η), above the equilibrium potential. Overpotential is a critical parameter for evaluating the activity of electrocatalysts. Other vital parameters for consideration include the overall electrode activity, Tafel plot, Faradaic efficiency, turnover frequency (TOF), and electrochemical stability.[7]

2.3.1. Overpotential

The water-splitting efficiency is typically assessed through techniques like linear sweep voltammetry (LSV) or cyclic voltammetry (CV). It's important to note that LSV or CV results are preliminary assessments, taking into account that the non-Faradaic capacitive current is part of the total current. In cases where the electrocatalyst demonstrates outstanding performance for both the HER and OER in the same environment, a complete water electrolyzer can be constructed. This electrolyzer utilizes the catalysts at both the cathode and anode in a two-electrode system with electrolytes such as KOH or H₂SO₄. Typically, the actual potential (overpotential) at a current density of 10 or 20 mA cm⁻² is compared. A lower potential voltage (overpotential) value indicates higher electrochemical activity (see Figure 2. 6).[7]

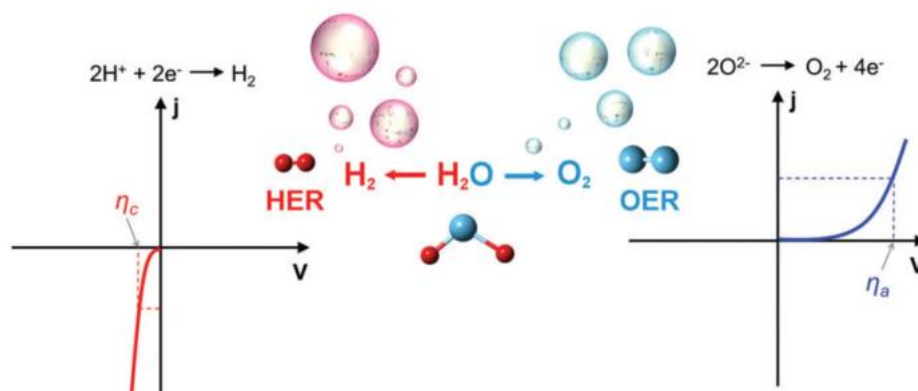


Figure 2. 6. Polarization curves for HER (left) and OER (right). The η_c and η_a are the overpotentials for cathode and anode at the same current (j), respectively.[6]

2.3.2. Tafel Plot

The Tafel plot is generated from the LSV outcome, focusing on the linear segment at relatively modest overpotentials, and fitting it to the Tafel equation ($\eta = a + b \log j$, where η represents the overpotential, j stands for the current density, and b represents the Tafel slope). This plot illustrates the correlation between the overpotential (η) and the

logarithm of the current density ($\log j$). It offers valuable kinetic insights into the reaction mechanism for a specific electrocatalyst. Another vital parameter, often considered as an indicator of the intrinsic electrocatalytic activity of materials at the reversible potential, is the exchange-current density (j_0). Calculating j_0 involves using the Tafel equation under the assumption that η is zero. In water electrolysis, a noteworthy criterion for a high-performance electrocatalyst is a low Tafel slope coupled with a high exchange current density (refer to Figure 2. 7).[7]

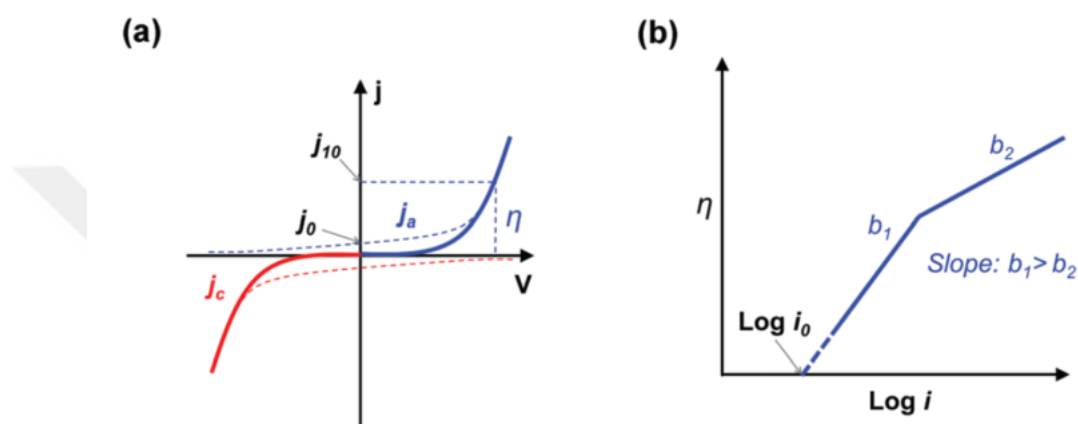


Figure 2. 7. a) Polarization curves for cathode (red) and anode (blue) electrode. j_0 is the exchange current when $j_a = j_c$. j_{10} is a commonly agreed value for one to report overpotential (η) at this current (assuming the area is 1 cm^2) value. (b) In the η vs. $\log j$ curve, the exchange current density (j_0) could be derived by extrapolating the curve to $\eta = 0$. Slope b is the Tafel slope, where it is usually assumed that the steeper (larger) the slope is, the worse the electrode kinetics will be (slower current increased in the same given potential comparing in the case of b_1 and b_2).[6]

2.3.3. Turnover Frequency (TOF)

The TOF, quantified as the quantity of reactant a catalyst can transform into a desired product per catalytic site within a specific timeframe, is an indicator of the intrinsic catalytic activity of each catalytic site. The TOF (s^{-1}) can be computed using the formula: $\text{TOF} = jA/\alpha Fn$, where j (mA cm^{-2}) denotes the current density for the sample at a given overpotential during the LSV measurement; A is the surface area of the working electrode; α represents the electron count of the target product (electrons/mol); F stands for Faraday's constant ($96485.3 \text{ C mol}^{-1}$); and n corresponds to the moles (mol) of coated metal atoms on the electrode calculated from m (g) divided by the molecular weight M

(g/mol) of the catalysts. Notably, not all atoms within a catalyst possess catalytic activity and may not be equally accessible. Consequently, obtaining a precise TOF value is challenging. Nonetheless, this parameter remains relevant and valuable for comparing the performances of similar catalytic materials.[7]

2.3.4. Faradaic Efficiency

Faradaic efficiency stands as another quantitative metric utilized for both the HER and OER. It can be defined as the electrocatalyst's effectiveness in transferring electrons provided by the external circuit across the interface to the electroactive species, consequently facilitating the electrode reaction (either the HER or OER in this context). Two methods are employed to determine the Faradaic efficiency. The first method involves the electrochemical approach utilizing a rotating ring disc electrode (RRDE), which is specifically applicable to the OER. In this method, the catalytically active material is coated on the disc of the RRDE without disturbing the ring. A commonly utilized RRDE comprises a glassy carbon (GC) disc and Pt ring. Prior to this, the collection efficiency of the RRDE must be known or experimentally determined by examining the response of the conventional ferrous/ferric redox system at various rotation rates. Subsequently, the potential at the disk is swept over the same experimental potential window of the OER, while simultaneously maintaining a constant potential at the Pt ring for the oxygen reduction reaction (ORR). The ORR potential at the Pt ring is adjusted based on the pH of the electrolyte solution. The equation below is employed to calculate the Faradaic efficiency (FE) of an OER catalyst.

$$FE = \frac{I_R n_D}{I_D n_R N_{CL}}$$

Here, I_R and I_D represent the current at the ring and disc, respectively. Additionally, n_R and n_D refer to the numbers of electrons transferred at the ring and disc, respectively, while N_{CL} stands for the collection efficiency of the utilized RRDE. This technique is highly valuable for accurately determining the activity of an OER catalyst, particularly in scenarios where the Faradaic efficiency might be compromised. Such situations include: an OER catalyst exhibiting one or more strong redox peaks within the potential window of the OER (a characteristic observed in nearly all Ni-, Co-, and Fe-based catalysts), an electrocatalyst capable of facilitating undesired side reactions, or an electrocatalyst that experiences heating during the electrocatalysis process.[8]

2.3.5. Stability

In addition to assessing the overall water splitting activity, long-term durability is a crucial factor in determining the practical viability for energy conversion and storage applications. Two commonly used methods evaluate this durability: the first method involves chronoamperometry (I-t curve) or chronopotentiometry (E-t curve). Here, a specific current density greater than 10 mA cm^{-2} or a potential at which the current density exceeds 10 mA cm^{-2} is maintained for an extended period, and the corresponding variation in potential or current density is recorded over time. The second approach entails conducting a recycling CV or LSV experiment. This requires performing over 1000 cycles at an accelerated scanning rate of 100 mV s^{-1} . The reduction in current density, as measured by LSV after a certain number of cycles, is used to assess the electrocatalytic stability performance. An electrocatalyst is deemed to possess exceptional stability for water splitting if minimal potential or current density variation is observed in the first approach, or if there is negligible loss of current density in the second approach.[7]

2.4. Electrocatalytic Materials

Certainly, significant endeavors have been directed towards enhancing the HER and OER efficiency through the development of nonprecious electrocatalysts. For instance, various materials such as metal alloys, borides, carbides, nitrides, phosphides, and chalcogenides have been investigated as effective HER electrocatalysts in acidic solutions. Similarly, numerous nonprecious OER catalysts, including metal oxides and (oxy)hydroxides, have been documented, demonstrating encouraging performance in alkaline environments.[5] The focus of this dissertation is transition metal borides (TMBs) and earth-abundant transition metal-based catalysts.

2.4.1. Transition Metal Borides

Recently, TMBs have garnered considerable attention within the realms of energy conversion and storage. A growing body of literature underscores the exceptional electrocatalytic capabilities of TMBs for water splitting. TMBs possess distinct properties for water splitting when compared to other TM-based components. To begin, within many amorphous TMB systems, the reverse electron transfer from boron to metals results in an electron-enriched environment at the metal sites, promoting electrochemical reactions. Additionally, the inevitable surface oxidation of TMBs leads to alterations in surface

chemistry through the formation of borates, boron oxides, TM oxides, and TM (oxy)hydroxides. These active species significantly influence catalytic reactions. Furthermore, annealing treatments can induce phase transformations in TMBs, shifting from an amorphous phase to a crystalline phase, profoundly impacting catalytic performance. Consequently, the advancement of TMB materials presents compelling catalysts for electrocatalytic water splitting. These research publications also furnish valuable insights into constructing high-performance TMBs electrocatalysts using advanced strategies such as doping, hybridization, phase/crystallinity engineering, and surface oxidation.[4]

TMBs are typically characterized by strong chemical, thermal, and mechanical stability due to their unique bonding features involving metal–metal, metal–boron, and boron–boron interactions. Some metal borides have been recognized for their exceptional physical properties, such as superconductivity and super hardness, for over a decade. However, it's only in recent years that the remarkable catalytic potential of borides has garnered research attention.

The somewhat delayed exploration of borides' catalytic capabilities is partly attributed to the scarcity of suitable boride samples conducive to catalytic investigations. Firstly, most boride samples with well-defined structures, including those utilized for studying physical properties, are prepared under extreme conditions like high temperature and high pressure. These boride samples typically consist of bulk particles in limited quantities, posing challenges for branching out into catalysis studies. Secondly, while a few methods exist to synthesize metal borides under milder conditions, the resultant samples often exhibit restrictions in elemental composition and crystal structure.

Thirdly, metal borides commonly exist in various phase variations with subtle stoichiometric differences, making the synthesis of phase-pure target products challenging. Therefore, the development of universal pathways for synthesizing phase-pure borides under relatively mild conditions is vital for discovering efficient boride catalysts.[9]

Metal diborides (MDbs), a subgroup of the large family of TMBs have very recently come into the picture for HER due to their higher electronic conductivity and density of active sites. Despite considerable signs of progress achieved in catalytic properties of MDbs towards HER, their electrocatalytic activities towards OER remained largely unknown.[10] The structures of over 30 members of the MDbs family are categorized into three types, namely AlB_2 -type, ReB_2 -type, and RuB_2 -type diborides. The critical

ingredients in the 3D framework are the 2D boron layers to which MDbs ascribe both their high electrical conductivity and high density of active sites. Concerning AlB_2 -type MDbs, boron layers are graphene-like borophene subunit sheets, for ReB_2 -type and RuB_2 -type MDbs boron layers are puckered-type subunits with respective “chair” and “boat” arrangements.[11] The crystal structures of twelve different monometallic MDbs including TiB_2 , VB_2 , CrB_2 , MnB_2 , ZrB_2 , NbB_2 , MoB_2 , HfB_2 , TaB_2 , WB_2 , ReB_2 and RuB_2 are shown in Figure 2. 8.

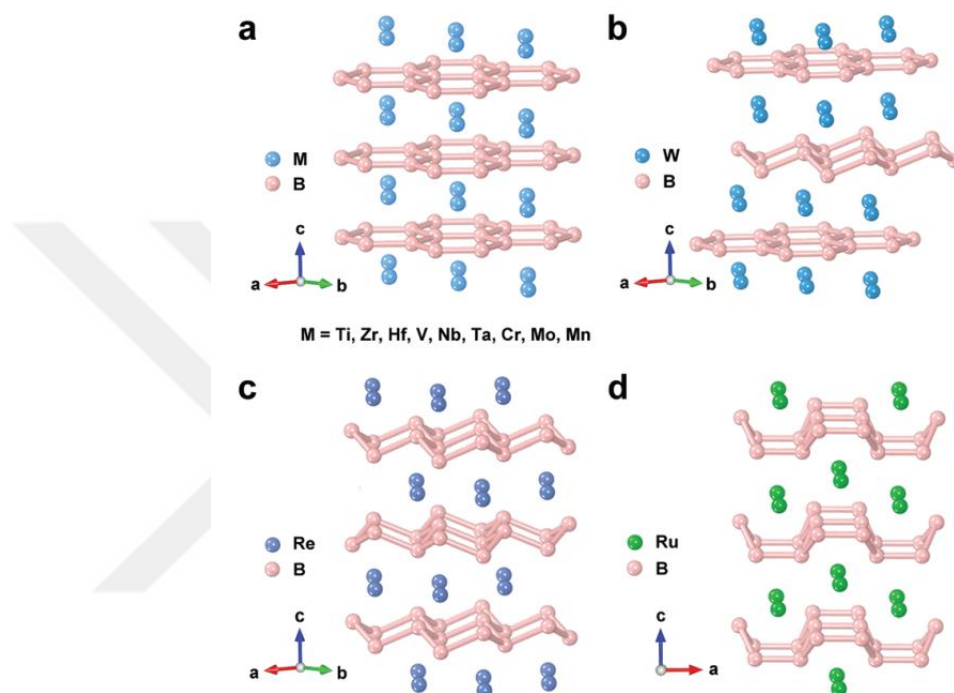


Figure 2. 8. The crystal structures of twelve metal diborides: (a) MB_2 ($M = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, \text{ and } Mn$), (b) WB_2 , (c) ReB_2 , and (d) RuB_2 . The pink balls represent boron atoms, whereas the light blue, blue, bluish violet and green balls represent the corresponding metal atoms.[9]

2.4.2. Synthetic Methods

Obtaining boride samples that are both phase-pure and suitable for catalytic studies poses a significant obstacle. This challenge is underscored by several factors:

(i) Conventional solid-state methods used to prepare borides with well-defined structures necessitate high temperature and pressure conditions. The resulting samples typically consist of bulk particles in limited quantities, making them suitable for studying physical properties but less conducive to the exploration of catalytic abilities.

(ii) While a few milder synthesis routes are utilized to produce borides, the resulting materials often have notable limitations in terms of elemental composition and crystal phase.

(iii) In the majority of metal–boron systems, multiple phases with subtle stoichiometric differences are present, presenting difficulties in the precise preparation of phase-pure borides for targeted catalytic investigations.

2.4.2.1.Element Reaction Route

The elemental reaction pathway stands as a prevalent approach for synthesizing borides. Under this synthetic approach, borides are generally acquired through the sintering of a mixture containing elemental metal and boron, either in a vacuum or an inert gas environment. The sintering process usually takes place in conditions of elevated pressure and temperature, employing high pressure–high temperature equipment or an arc-melting chamber.

2.4.2.2.Thermal Reduction Route

This approach encompasses numerous chemical reaction types, frequently employing metal oxides, halides, or sulfides as sources of metal. The method leverages a diverse range of reducing agents, enabling the development of various established reactions such as solid-state metathesis and metallothermic reduction. These reactions facilitate straightforward, swift, or universally applicable synthesis of borides.

2.4.2.3.Boron Source as the Reducing Agent

Key reducing agents containing boron include elemental boron, boranes, borohydrides, and alkaline-earth borides. These agents function within diverse reaction systems, resulting in the formation of borides with varying crystallinities and morphologies. For instance, certain boranes (such as B_2H_6 , B_5H_9) as volatile precursors have been utilized in chemical vapor deposition (CVD) to synthesize boride nanowires. On the other hand, borohydrides (e.g., KBH_4 , $NaBH_4$) have been widely applied in solution-based synthesis approaches to produce amorphous or low crystalline boride nanostructures. Additionally, elemental boron and alkaline-earth borides (e.g., MgB_2) have been employed in solid phase reduction of metal sources, resulting in the formation of boride particles.

2.4.2.4.Introduction of an Extra Reducing Agent

In certain boride synthesis processes, the introduction of an additional reducing agent (such as carbon, hydrogen, or a metal) is imperative. Carbothermal reduction, one of the

earliest techniques for boride synthesis, often necessitates this step. However, this method frequently faces challenges related to carbon, boron, or boron carbide contamination in the resulting samples, limiting its widespread application.

On the other hand, hydrogen can fulfill a dual role as both a carrier gas and a reducing agent for the boron source. Consequently, it offers advantages in the production of high-quality boride layers using the CVD technique. For example, Wang et al. recently achieved the fabrication of ultrathin 2D Mo_3B films on Mo foils by utilizing hydrogen to transport the boron/boron oxide mixture as the boronizing agent (as depicted in Figure 2.9).[12]

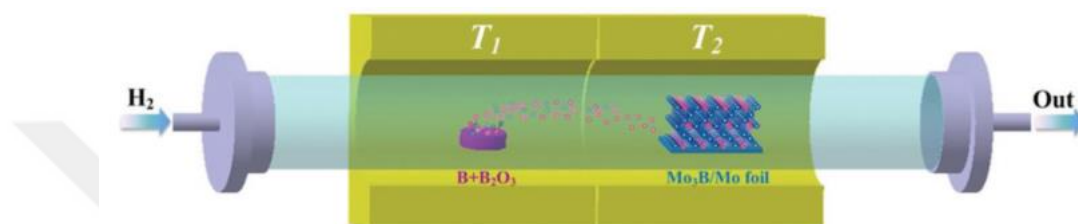


Figure 2. 9. Schematic diagram of the growth of Mo_3B layers on Mo foils.[12]

2.4.3. Transition Metal Oxides

The relentless pursuit to replace highly active but not stable noble metal-based electrocatalysts has created a surge of research on the design and development of materials involving earth-abundant elements with which not only high-performance can be expected but also durability can be perceived.[3] So far, a miscellaneous series of transition metal (TM: Fe, Co, Ni, Mn, Cu, V, Cr) based catalysts including but not limited to phosphides, oxides, oxyhydrates, perovskites, nitrides, borides, and sulfides[13-18] have been architected to simultaneously catalyze both HER and OER. Transition metal oxides (TMOs) due to their high abundance, multi-valence state, intrinsic activity, and rich redox properties [15, 16, 19] can rival the noble metal-based catalysts and even surpass them in some cases. Beyond the preceding merits, TMOs possess some additional values such as sufficient tolerance against corrosion within a wide range of electrochemical window in alkaline solutions[7] and containing abundant structural defects[20] which make them excellent candidates for OER, HER, and overall water splitting. Moreover, it has been reported that binary/ternary TMOs could promote the kinetic of water splitting, ascribing to the peculiar morphology grown on the surface for facilitated ion transfer,[21] creating distinctive crystal/crystal interfaces for better

adsorption/desorption of intermediates,[22] improved electronic conductivity,[23, 24] and the effect of synergy between multiple metal centers.[24]

Recently, there has been a surge of interest in the electrochemical properties of bimetallic oxides in comparison to single-component oxides due to their improved characteristics [25-27]. Bimetallic oxide catalysts could alter the electronic structures of the catalysts by regulating the composition, physical, and chemical aspects of the metals in the structure [28, 29]. Moreover, bimetallic oxides offer multiple active sites, trap inactive active sites, and elevate the conductivity at the same time [28, 30]. TM molybdates as a subgroup of bimetallic compounds have received much attention because of their high electrochemical activities which can be ascribed to their rich polymorphism and high conductivity originating from metal molybdates [26, 31]. CoMoO_4 is considered a potentially good electrocatalytic material owing to the synergy between the redox ability of Co and the high adsorption capacity of Mo in its framework [26, 32-34]. Yet, CoMoO_4 shows limited HER performance in alkaline media which is most probably attributed to its poor intrinsic conductivity. Thus, it is a significant task to modify the electrocatalytic features of CoMoO_4 to act effectively in alkaline HER [35].

Multiple strategies have been introduced to promote the conductivity and electrocatalytic properties of materials that include phase transition [36, 37], coupling with highly conductive carbon materials, doping with heteroatoms [38], strain engineering [35, 39], facet control [40], and oxygen vacancies [41, 42]. Among them, elemental doping is a common way to optimize the physicochemical properties of catalysts and thereby adjust the electronic structure, which could availably improve HER performance [43-45].

The HER performances of Pt-based catalysts under alkaline conditions are determined by their capacity to bind hydroxyl species (OH^*),[47, 48] and the optimization of the alkaline HER process can be acquired by regulating the binding energies of reactants (OH^* and H^*) on dual active sites.[49-51] Similar analogy can be evinced for TM-based catalysts to minimize the kinetic barrier of the Volmer step in alkaline media by adding or designing dual active sites in the catalyst to separately fine-tune the binding energy of reactants (OH^* and H^*). One way to address this issue is to develop catalysts that combine metal and metal oxides. These catalysts can cleave the H-OH bond with the help of the oxides while the metal component helps to adsorb and recombine the resulting H^* intermediates into molecules. According to the calculations performed by Zhou et al.[52] using DFT, it was shown that the dual active sites at the

interfaces of NiO/Ni heterostructure—consisting of metallic Ni sites and oxygen vacancies-modified NiO sites—have adsorption preference toward H^* and OH^* , individually, facilitating the water adsorption and alleviating the water cleavage with a lower energy barrier of 0.31 eV in Volmer step for NiO/Ni heterostructure compared to the individual components of Ni (0.47 eV) and NiO (1.42 eV) catalysts.[52] Moreover, oxygen vacancies can act as electron donors (n-type defects) and accelerate the electron transfer process. Furthermore, oxygen vacancies can modify the electronic structure of metal oxide, thereby improving its electrical conductivity.[53]

Ni-based materials have gained popularity as electrocatalysts for alkaline HER because the energy required for hydrogen binding is closer to that of Pt.[54] Furthermore, the open literature has shown that alloying Ni with other metals such as Ru,[55] Cu,[56] Zn,[57] Fe, Co, and Mo can further boost catalyst's activity for HER owing to their synergistic optimization of active edge sites and excellent corrosion resistance to basic environment.[58, 59] NiMo alloys; however, have been found to be particularly effective for HER due to their intrinsic activity and favorable hydrogen binding energy.[60] Yet, the overall performance of NiMo alloy alone is not optimal, resulting in low efficiency and high energy consumption. Thus, it is of the utmost importance to promote the catalytic behavior of NiMo alloy.[60] Besides heterostructure engineering, a different approach is to enhance the HER performance by increasing the specific surface area. To do so, researchers have utilized various substrates as supports for NiMo alloys electrode with high specific areas such as Ni foam (NF), Cu foam, carbon cloth, and Ti mesh.[61, 62] In this study, a heterostructure composed of a metallic-like component (NiMo alloy) and an oxide ($CoMoO_4$) was fabricated directly on a NF substrate.

2.4.4. Metal Organic Frameworks (MOFs)

Despite the numerous advantages of 3d TM-derivative materials, their performance under strong basic/acidic conditions and high current densities is limited[19] and thus not practical for real applications. To overcome this impediment, the construction of a composite with other materials such as metal organic frameworks (MOFs) with inherent mechanical stability could be a promising solution.[63-65] MOFs, a newly emerged family of crystalline coordination polymers composed of metal ions (e.g. Fe, Co, Ni, Cu) attached to organic ligands with tunable chemical composition, high electrochemical surface area, hollow structures, and controllable morphology,[14, 19] have gained fame

for a variety of applications such as electrocatalytic water splitting,[66-68] gas storage,[69, 70] chemical sensing,[71, 72] supercapacitors,[73, 74] and metal-air batteries.[75-77] Regarding catalysis, the unstable coordinated solvent molecules in the MOF structure can easily detach in the course of the reaction and form coordinatively unsaturated metal centers (CUMCs).[78] Depending on coordinated metal components, the CUMCs may function as typical Lewis acid centers to demonstrate versatile catalytic activities. Yet, the poor electrical conductivities of MOFs (about 10^{-10} S m⁻¹)[79, 80] hamper their implementation in practice as efficient electrocatalysts for the OER and HER.[81-83]

To address the above-stated issue one approach is to load electrocatalytic MOFs on conductive substrates such as NF. The three-dimensional (3D) open porous framework of NF with a large specific surface area and zigzag channels can further strengthen the electron and mass transport of in-situ grown MOFs on the NF backbone.[3] In fact, self-supported MOF electrocatalysts induce superior electrochemical performances compared to the powder-based systems with the binders such as Nafion,[14, 84, 85] which can be attributed to the synergistic effect between MOF-based composites and conductive host.[86] Additionally, the idea of binder-free hydrothermal synthesis of both ternary mixed TMOs and MOFs using NF as a substrate is interesting in that NF can function as a current collector for direct growth. Moreover, this strategy can minimize binder costs, reduce preparation time, boost ion transport, and strengthen the contact between electrocapacitive material and substrate.

2.4.5. Basic Strategy for Designing of Self Supported MOF

MOFs represent crystalline porous materials where metal centers are interconnected by organic bridging ligands through coordination bonds. Extensive exploration has been conducted on various MOFs, encompassing different compositions, deliberately designed morphologies, high porosity, and a significant electrochemical surface area. MOFs can be deliberately synthesized to exhibit core-shell and hollow structures. Furthermore, the properties of MOFs can be fine-tuned through post-synthetic modifications. These materials offer several advantages, including:

i) Cost-effectiveness based on the use of readily available transition metals from the earth's abundant resources. ii) Ease and simplicity in their synthesis process. iii) Tailoring of properties with a specific desired morphology.

Moreover, MOFs possess distinctive structural and electronic properties, rendering them ideal for utilization as sacrificial templates in the synthesis of functional materials. This utility stems from:

i) Controlled design and the potential for post-synthetic modifications. ii) The beneficial role of organic ligands in the synthesis of carbon-based materials. iii) The ability to incorporate heteroatoms (C, N, P, and O) to enhance catalytic activity.

The makeup, structure, porosity, and crystal arrangement of MOFs are contingent on the coordination between the bridging organic ligands and the metallic building blocks. Typically, first-row transition metals (V, Cr, Mn, Co, Ni, Fe, Cu, Zn) have been employed as central metal units in the synthesis of MOFs. A diverse array of bridging ligands, such as aromatic carboxylic acids, imidazoles, and cyanometallate reagents, have been utilized to tailor and fine-tune the characteristics of MOFs. The comprehensive structure of MOFs can be steered by the coordination environment, geometry, and electronic configurations of the metal centers. Additionally, successful synthesis of multi-metallic MOF systems has been achieved, demonstrating deliberate control over morphology and compositions.

MOFs are not directly suitable for serving as catalysts in electrochemical water splitting due to their inadequate electronic conductivity, limited mass permeability, and obstruction of active sites by organic linkers. Furthermore, they exhibit low stability in an electrolytic environment. Capitalizing on their distinctive properties, MOFs have been effectively utilized as precursors to develop catalyst systems for electrochemical water splitting. A range of catalytically potent materials, such as metal oxides, metal phosphides, metal sulfides, and metal selenides, have been derived from MOFs, demonstrating exceptional performance in electrochemical water splitting. Primarily, MIL (Materials Institute Lavoisier), ZIF (Zeolitic Imidazolate Framework), and PBA (Prussian Blue Analogue) are employed as precursor frameworks in the synthesis of these functional materials (as depicted in Figure 2. 10).

These catalysts derived from MOFs also face challenges regarding mechanical stability and electronic conductivity, especially when applied on solid supports using binders. To address these limitations, self-supported MOFs have been recently introduced as precursors for the synthesis of self-supported MOF-derived catalysts. Two primary strategies are employed in the synthesis of self-supported MOFs: i) hydrothermal/solvothermal synthesis and ii) template-directed synthesis. MOFs are synthesized using either a room temperature method or under high temperature and pressure in an autoclave by combining a metal salt solution and an organic linker with a

3D-support. The reaction conditions significantly impact the morphology, size, and structure of the resulting MOF. For instance, Sun et al. utilized terephthalic acid and Ni, Fe metal salt to synthesize NiFe-MOF on nickel foam using a hydrothermal method in an autoclave. Similarly, Co-ZIF was synthesized on carbon cloth at room temperature by treating a cobalt solution with 2-methyl imidazole.[14]

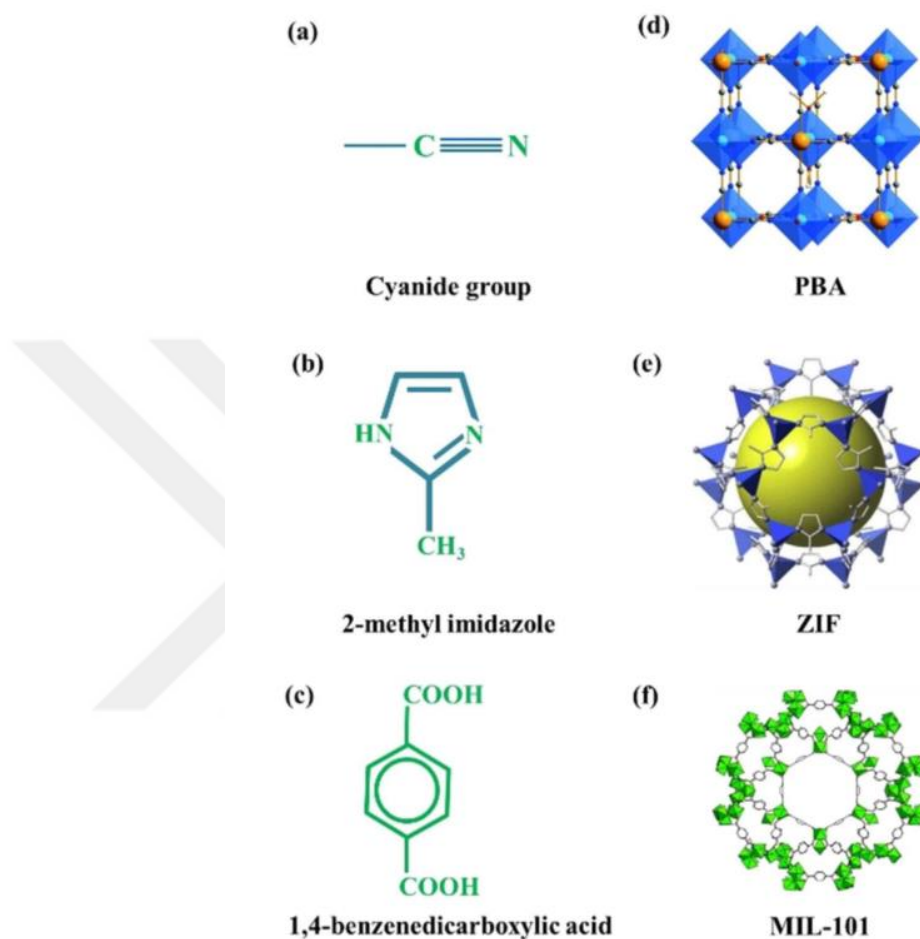


Figure 2. 10. a,b,c) Different types of bridging ligand utilized for the synthesis of metal organic framework and d,e,f) structure of the corresponding MOFs.[14]

Both strategies for designing self-supported MOFs come with distinct advantages and disadvantages. In hydrothermal/solvothermal synthesis, the specific synthetic conditions significantly influence the crystallization process. While altering the reaction conditions allows control over morphology and crystal growth, a notable drawback of this method is the relatively weak interaction between MOF and the solid support. This has raised concerns regarding its effectiveness.

Conversely, template-directed synthesis was embraced to establish a robust interaction between MOF and the solid support. This method allows for the achievement of a strong MOF-solid support connection. Template-directed synthesis can be conducted

at comparably low temperatures (even at room temperature) and atmospheric pressure, but it doesn't afford the same level of control over morphology and crystal growth. It's worth noting that in several instances, achieving a complete conversion of the template into a self-supported MOF was challenging.

2.4.5.1. Designing of Self-Supported MOF Derived Catalysts

Self-supported MOFs have found application as the initial materials to create functional, self-supported MOF-derived materials, showcasing outstanding performance in electrochemical water splitting. These self-supported MOFs can be converted into functional materials using three primary promising strategies: i) the hydrothermal/solvothermal strategy; ii) calcination and chemical vapor deposition; and iii) electrochemical transformation.

2.4.5.2. Hydrothermal/Solvothermal Synthesis

To achieve hydrothermal synthesis of a catalyst derived from self-supported MOFs, the self-supported MOF precursor is heated in an autoclave with diverse reagents (as depicted in Figure 2. 11). Solvents such as water or ethanol, in combination with different reagents like sulfur, phosphorus, selenium, and others, have been employed to facilitate the transformation of self-supported MOFs into MOF-derived materials. The resulting morphology and crystallization of the catalysts derived from self-supported MOFs are notably influenced by the reaction conditions.

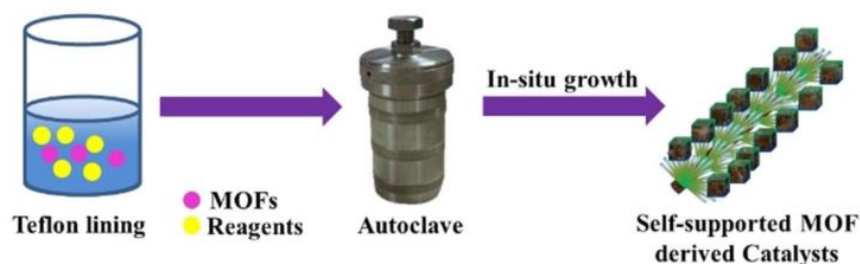


Figure 2. 11. Synthesis of self-supported MOF derived catalysts by hydrothermal method using self-supported MOF-precursor.[14]

2.4.5.3. Calcination and Chemical Vapor Deposition (CVD)

Calcination stands as the most promising method for synthesizing metal oxides derived from self-supported MOFs. This process involves subjecting the self-supported MOF precursor to high-temperature heating in the presence of air. MOFs contain a sufficient amount of carbon and nitrogen, which can be oxidized during air calcination, resulting in the creation of porosity in the oxide materials. For instance, CoFe-PBA@NF was subjected to heating at 350 °C to synthesize CoFe₂O₄@NF. During this process, the

CN bridging of the PBA was burned, resulting in the formation of a porous self-supported $\text{CoFe}_2\text{O}_4@\text{NF}$ catalyst. Similarly, $\text{NiFe-PBA}@\text{NF}$ was also calcined in the presence of air to produce the $\text{Fe-NiO}@\text{NF}$ catalyst.

In the CVD process, self-supported MOF precursors undergo treatment with various sulfur, selenium, and phosphorus reagents at elevated temperatures within an inert atmosphere (as illustrated in Figure 2. 12). For instance, self-supported PBAs and ZIFs have been utilized as the initial materials for synthesizing metal phosphides, metal sulfides, and metal selenides.

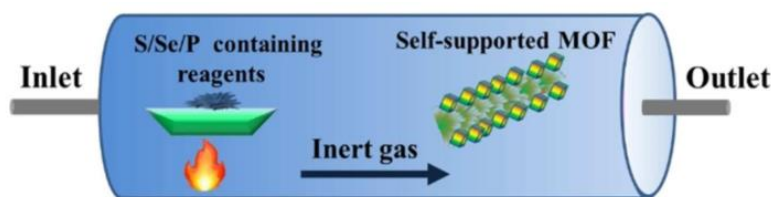


Figure 2. 12. Synthesis of self-supported MOF derived catalysts using CVD technique.[14]

2.4.5.4. Electrochemical Transformation

The electrochemical transformation of self-supported MOFs into layered metal hydroxides/metal (oxy)hydroxides has been recently documented (depicted in Figure 2. 13). During the electrochemical water splitting, the anodic oxidation of self-supported MOFs leads to the formation of an active catalyst comprised of metal hydroxide-(oxy)hydroxide. In this process, the self-supported MOF acts as a template for the electrochemical transformation into a self-supported metal hydroxide-(oxy)hydroxide active catalyst.

This mixed-phase active catalyst augments the number of available active sites, facilitates rapid mass transfer, and enhances electronic conductivity.

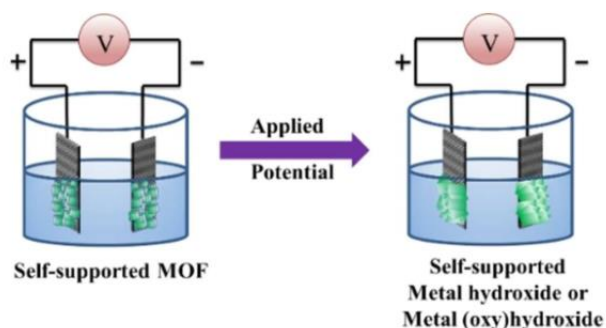


Figure 2. 13. Electrochemical transformation of self-supported MOF into metal hydroxide-(oxy)hydroxide nanosheets with applied potential.[14]

CHAPTER 3

METAL DOPED LAYERED MgB₂ NANOPARTICLES AS NOVEL ELECTROCATALYSTS FOR WATER SPLITTING



The majority of this chapter has been published in *Scientific Reports*, 2021, 11(1), 3337. The original manuscript has been rearranged to conform to the format requirements of the dissertation.

3.1. Introduction

In the last few years, plenty of non-precious transition metal compounds, namely sulfides (NiS₂, FeS₂, CoS₂), phosphides (Ni₂P, FeP, CoP), and selenides (CoSe₂, FeSe₂) have been found with excellent HER activities.[87, 88] Recently, TM (Ni, Co, Fe, etc)-based borides have sparked considerable attention in the fields of energy conversion and storage. An immense growing number of studies evince that some traits introduce TMBs as exceptional electrocatalysts for water splitting.[89, 90] As compared to other TM-based components, TMBs possess some special attributes such as high chemical, thermal, and mechanical stability, significant catalytic activity, and conductivity for water splitting.[4, 91] In this sense, the results of several recent studies confirm the potential of transition metal borides as dual-functional catalysts for water splitting;[92] yet, among TMBs, MDbs have been poorly explored for this application.

Metal diborides known by the general formula of MB₂, feature some intrinsic singular characteristics including hardness, chemical durability, high thermal conductivity, and high electrical conductivity.[93, 94] So far, MgB₂, as a representative of the large family of MDbs has been a well-known material for its superconductivity at low temperatures.[95, 96] MgB₂ has other attractive characteristics as regards practical use, such as the ability of doping effect, low cost, and abundance of its raw materials, all of which makes it an auspicious candidate for doping and subsequently utilizing in water splitting.[97] Moreover, a singular property of MgB₂ is the evacuation of B 2p-s bands on the basis of a unique Mg-B interaction. Accordingly, for any MDdb, the correlation between boron and the metal atoms plays a decisive role on effectiveness of its properties leading to a firm premise for effective application in water electrolysis.[98]

Herein we examine and report a very successful approach to substitute the divalent transition metals in Mg_{1-x}Tm_xB₂ ($x = 0.025, 0.05$, and 0.1 ; $Tm = Fe$ and Co) for the Mg²⁺ as primarily enhanced HER electrocatalysts under alkaline medium. It should be pointed out that the aforementioned electrocatalysts have also been tested as OER catalysts and the data are provided in the supporting information.

3.2.EXPERIMENTAL SECTION

3.2.1. *Synthesis of Electrocatalysts*

3.2.1.1.Preparation of MgB₂

In general, there are two methods to synthesize magnesium diboride, namely “in situ” and “ex-situ” techniques. In this study, the former method has been preferred to the latter due to the conspicuous benefits. In the “in situ” technique, precursor materials are mixed with stoichiometric compositions and annealed under the inert condition. Compared to the “ex-situ” technique, “in situ” is more effective for doping purposes, since already reacted powders of MgB₂ are used in the “ex-situ” technique which does not leave enough room to develop metal doping.[96] Further, according to the literature,[96] “ex-situ” fabrication of MgB₂ is usually subjected to poor grain conductivity which hinders its application in electrolysis. In brief, the synthesis of pure MgB₂ powders was carried out via the “in situ” process. A specified amount of magnesium powder (Mg, 99.8%; Alfa Aesar) and amorphous nano boron (B, 98.5%; Pavezyum) were mixed in stoichiometric amounts in a glove box under Ar atmosphere and transferred into a steel tube. Afterward, the steel tube was sealed by arc melting under Ar. Then, the annealing process was applied at 850 °C for 6 h. It should be mentioned that following the annealing process, powders were ground in an agate mortar to obtain fine and homogenous powders for the electrochemical measurements.

3.2.1.2.Preparation of Mg_{1-x}Tm_xB₂ (x = 0.025, 0.05, and 0.1; Tm = Fe and Co)

For the substitution experiments, cobalt powder (Co, 99.8%; Alfa Aesar), and reduced fine powder of iron (Fe, ≥99%, Sigma-Aldrich), were utilized individually. The powders: Mg, Fe (or Co), and B with the formal composition of Mg_{1-x}Tm_xB₂ were homogenized by grinding in an agate mortar and then compacted into pellets with a diameter of 10 mm at a pressure of about 10 ton. The pellets were then sealed inside a steel tube and went under heat-treatment at 850 °C for 6 h. The post-annealing process is the same as bare MgB₂ (refer to Figure 3. 1).[99]

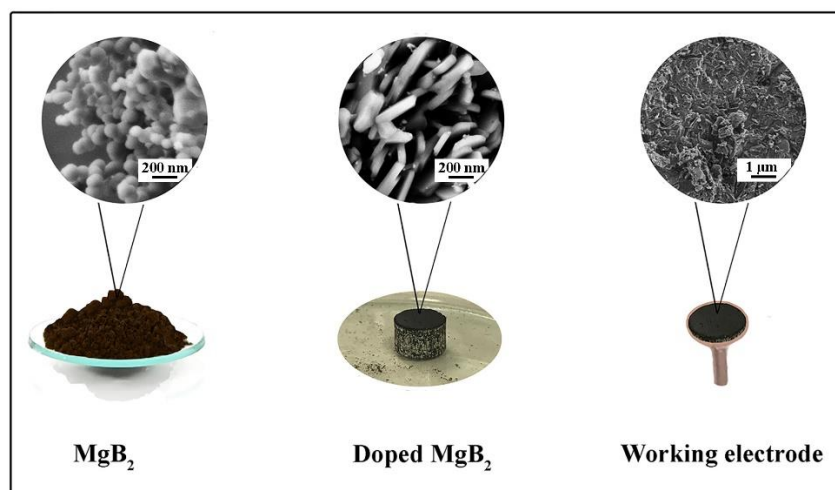


Figure 3. 1. Illustration of final states of MgB_2 powder, doped MgB_2 pellets, and the working electrode.

3.2.2. Apparatus and Procedure

3.2.2.1. Apparatus

The crystal structure and the phase purity analysis of the samples were carried out by X-ray diffraction (XRD, Rigaku Mini Flex 600) with $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation (40 kV voltage and 15 mA). Diffraction patterns were collected between 20° and 85° of 2θ . A zero-background powder specimen holder was utilized for the XRD analysis of all samples. The lattice parameters were refined using the WinCSD program package⁶⁵. High-resolution X-ray photoelectron spectroscopy (XPS) was performed with a Thermo K-Alpha with an $\text{Al K}\alpha$ source. The fittings were accomplished with Avantage software. All peaks were corrected with respect to the C 1s peak at 284.5 eV. For the analysis of the microstructure and surface morphology coupled with chemical composition, Field Emission Scanning Electron Microscopy (FESEM) equipped with Energy Dispersive X-ray spectroscopy (EDX) analyses were employed by Zeiss Ultra Plus Field Emission Scanning Electron Microscope using accelerating voltages of 5 and 12 kV, separately.

3.2.2.2. Electrochemical Measurements

Electrochemical measurements of the prepared electrocatalysts were conducted in a 1 M KOH solution using a three-electrode cell equipped with standard Reversible Hydrogen Electrode (RHE; HydroFlex®) as reference electrode and Pt wire as a counter electrode. All experiments were evaluated at room temperature using an AutoLab Potentiostat Galvanostat (PGSTAT302N, made in the Netherlands). The working

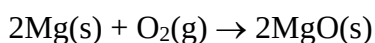
electrodes were made on a copper foil with a surface area of 0.35 cm² via deposition of powders through a polymeric binder. In brief, 30 mg of powders were mixed with a drop of the polymeric binder (paraffin wax) at about 100 °C and anchored on the copper foil supported by copper wire with a diameter of 1 mm. Then, the mixture was dried at ambient temperature. Finally, the designed electrodes were covered by a tubular plastic to prevent any contact with the solution. It is worth noting that the powder was dispersed uniformly on the foil and covered the whole area completely. For the electrochemical measurements, 0.5 g (powder) per mL (solution) was used for each electrode (see Figure 3. 1).

For electrochemical measurements, each sample underwent open circuit potential (OCP) measurements for 900 s to stabilize in the electrolyte. Then electrochemical impedance spectroscopy (EIS) was used to evaluate the charge transfer process as the critical factor determining the electrocatalytic activity on the electrodes. The OCP potential was recorded from a frequency of 100 kHz to 0.1 Hz with a 10 mV rms sinusoidal modulation. Afterward, the HER electrocatalytic activity was measured by applying LSV method from -0.2 to -1.6 V vs RHE at a sweep rate of 5 mV.s⁻¹ towards HER catalysis. Also, overpotential calculation was performed at -10 mA cm⁻² as an index of HER performance. For the OER, LSV was recorded at the same rate as HER from 0 to +1.8 V vs RHE towards OER catalysis.

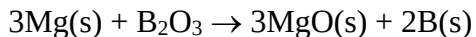
3.3.RESULTS AND DISCUSSIONS

XRD patterns of pure MgB₂, Co-doped MgB₂, and Fe-doped MgB₂ are illustrated in Figure 3. 2. For comparison, the theoretical diffraction pattern of magnesium diboride has also been included.[96, 100] Reflections shown in the theoretical pattern have appeared in both undoped MgB₂ as well as Mg_{1-x}Tm_xB₂ which confirms the successful synthesis technique applied in this study. However, there are trace amounts of labeled intrinsic impurities such as MgO (marked by #) at 2θ of 36.7°, 62.38° and Mg (marked by *) at 32.28°, 34.52°, 47.86°. Based on the literature,[96] two main paths that lead to the formation of MgO are as follows.

- If Mg precursor powder is sintered under oxygen it will produce MgO according to the following reaction:



- Also, the reaction of B₂O₃ with Mg forms MgO based on the following reaction:



Because all the synthesis procedure was carried out in a glovebox, the probable occurrence of above-mentioned reactions can be attributed to the impurity of precursor materials. Therefore, it is ironically interesting that the raw materials of Mg powder have surface oxide to some extent that produces MgO which is utterly inevitable to prevent from happening.

The X-ray diffractograms of Co-doped MgB₂ showed that there was no sign of secondary phases containing Co that is an obvious indication of successful substitution of Co for Mg in the crystal structure (see Figure A1 and Table A1). Nevertheless, weak peaks corresponding to Mg and MgO are still present with much lower intensity compared to MgB₂.

The X-ray diffraction for the samples with formal composition Mg_{1-x}Fe_xB₂ revealed that Mg and MgO peaks were roughly negligible. However, there were secondary phases at 2θ of 32.54°, 37.7°, and 45.08° which were assigned to the FeB phase. It is remarkable to mention that the impurity peak at 45.08° (labeled by •) can also be related to Fe₂B, especially at high concentration doping of Fe ($x = 0.1$).[101]

The minor amount of impurities with infinitesimal peaks indicated that the substitution of Co and Fe for Mg has significantly suppressed the amount of Mg and MgO formation. Moreover, with increasing Co and Fe content from $x = 0.025$ to 0.1 , the amount of impurities decreases as well, leading to finer structures that are obviously as a result of lowering the amount of Mg in the composition. Altogether, Mg_{0.95}Co_{0.05}B₂ contains the least amount of impurities.

The full-width-at-half-maximum (FWHM) values for synthesized catalysts were calculated by Program STOE WinXPOW (Darmstadt: Stoe & Cie GmbH, 2016) and subsequently crystallite size computed and summarized in Table 3.1. It is noteworthy to state that the FWHM of the XRD (101) peak has a direct relation with the concentration of Fe and Co dopants. This demonstrates that nano Fe- and Co-doped samples contain tiny grains and imperfect crystallinity. The Scherrer's equation is applied to calculate the average particle size (D) of the nanoparticles for each sample (peak (101))

$$D = (k \lambda) / (\beta \cos \theta)$$

where $k = 0.94$ is the shape factor of a particle, presuming shape of the nanoparticles as sphere, $\lambda = 1.5406 \text{ \AA}$ the wavelength of Cu K α radiation, β is the FWHM of the XRD (101) peak, and θ is the diffraction angle of the peak.[101] A glance at the table points

out that the average grain size of the parent MgB₂ is about 29 nm. These results based on the calculation of the grain size of doped samples unveils that doping concentration and grain size have reverse relation. By increasing doping amounts in both Fe and Co compositions, grain size shrinks.

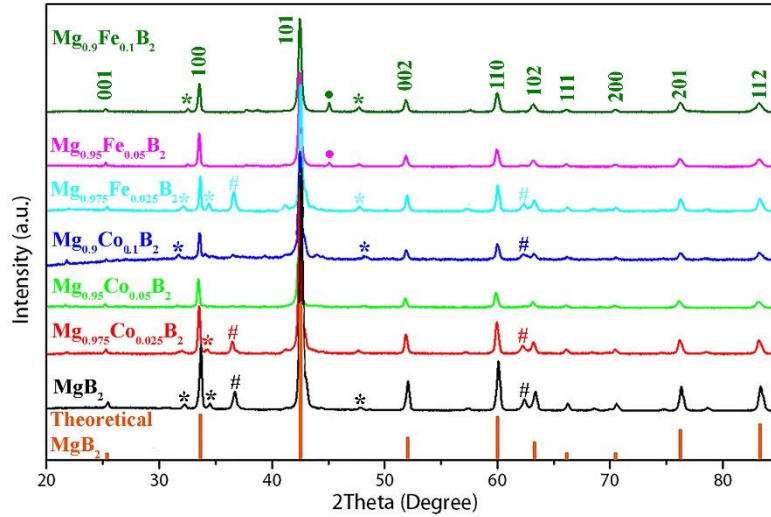


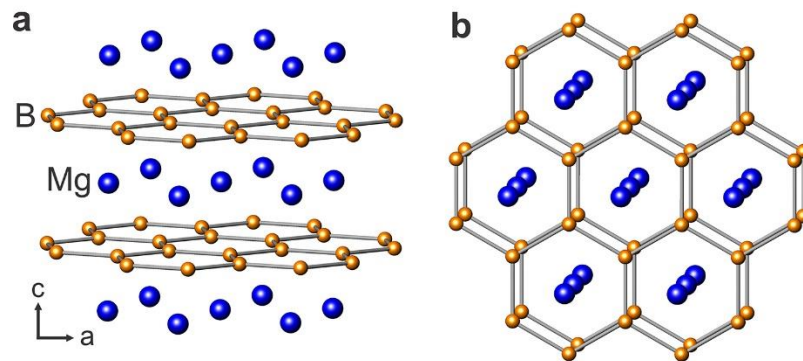
Figure 3. 2. XRD patterns of MgB₂ and Mg_{1-x}Tm_xB₂ ($x = 0.025, 0.05$, and 0.1 ; Tm = Fe and Co): impurity peaks of Mg, MgO, and FeB/Fe₂B are marked by *, #, and •, respectively.

Regarding previous experimental and theoretical results,[102] MgB₂ crystallizes in the well-known AlB₂-type structure with *P6/mmm* symmetry. As can be seen from Figure 3. 3, Mg layers are positioned between two honeycomb layers of B atoms. This structure resembles graphite regarded as that of completely intercalated graphite with carbon substituted by boron. Notwithstanding similarities, the B–B bonding is strongly anisotropic for the reason that intralayer B–B bonds are much shorter than the interlayer distance—which is not observed in graphite.[102]

Table 3. 1. FWHM values and crystallite size for pure Mg_{1-x}Tm_xB₂ ($x = 0.025, 0.05$, and 0.1 ; $Tm = Fe$ and Co).

Sample	FWHM (101)	D (nm)
MgB ₂	0.3087	28.82945
Mg _{0.975} Fe _{0.025} B ₂	0.2233	39.85514
Mg _{0.95} Fe _{0.05} B ₂	0.2447	36.36965
Mg _{0.9} Fe _{0.1} B ₂	0.2909	30.59351
Mg _{0.975} Co _{0.025} B ₂	0.2232	39.87299
Mg _{0.95} Co _{0.05} B ₂	0.2298	38.72782
Mg _{0.9} Co _{0.1} B ₂	0.3062	29.06483

Partial filling of two σ bands associated with strongly covalent sp^2 -hybrid bonding within the 2D boron layers is another attractive feature of MgB₂. The crystal structure manifests that the holes at the top of these σ bands possess mainly two-dimensional properties and are restricted within the boron sheets. On the contrary, electrons and holes in the π bands mostly represent 3D characteristics which are distributed through the whole crystal. Because of the extensive overlapping that takes place between all p orbitals (in-plane as well as out-of-plane) for adjacent boron atoms, σ and π bands encompass strong in-plane dispersion. However, the interlayer overlap, particularly for p_{xy} orbitals, are not large enough in such a way that the k_z dispersion of σ bands does not surpass 1 eV. It should be noted that unfilled σ bands in conjunction with boron p_{xy} character sufficiently maintain the covalent structure throughout the whole crystal.[103] Conducting covalent bonds stand for a distinctive feature of MgB₂ turning it into an exceptional material probably existing at the threshold of structural instability.[102]


 Figure 3. 3. Schematic design of layered MgB₂ structure. a) along the a-axis, b) along the c-axis.

The refined lattice parameters of MgB₂ and doped samples are tabulated in Table A2. The substitution of Mg²⁺ with Fe²⁺ and Co²⁺ leads to slightly higher lattice parameters due to the larger ionic radii of the transition metal ions (74.5 pm and 78 pm, respectively) compared to Mg²⁺ (72 pm).[104]

Figure 3. 4 and Figure A2 show XPS studies of pure MgB₂, Co-doped MgB₂, as well as Fe-doped MgB₂ nanoparticles. For this, Mg 1s, B 1s, Co 2p, and Fe 2p spectra have been analyzed. Besides, O 1s spectra have also been considered explaining the trace amount of surface impurities such as MgO. Regarding the fact that the Ar atmosphere was applied in all synthesizing steps, the reaction of B₂O₃ with Mg (as mentioned in the previous section) is inevitable. So, MgB₂ is somewhat vulnerable to oxidation as observed in Figure 3. 4 and Figure A2 O 1s spectra. As it was stated in the literature, several authors, including Corneille et al.[105] have reported two major peaks pertaining to O 1s and peroxide at 530.5 and 532–533.5 eV, separately. Likewise, several publications witnessed two-constituent peaks in the O 1s core-level spectrum, the lower binding energy peak at 531.0 ± 0.2 eV was ascribed to the MgO oxygen atom (O²⁻).[106] The higher binding energy O 1s constituent at 533.2 eV was indexed to chemisorbed OH⁻ at MgO (100).[106] Sanz et al.[107] and Sanz et al.[108] have also individually detected only one O 1s respective peaks at 531.2 and 530.5 eV, without any shoulder peak.[109] The emergence of any shoulder peak reported by some authors was on the account of their samples' growth procedures or conditions.[109] Considering the above-mentioned references, the major peak observed in this work corresponds to MgO at the binding energy of 531 eV. It should be noted that there is a minor shift in this peak position for Mg_{0.9}Fe_{0.1}B₂, which is within the accuracy of XPS measurements and data processing.

Fitting and deconvolution of Mg 1s spectra of pure MgB₂, reveals a peak at 1303.7 eV. Based on the literature,[110] metallic Mg shows a peak of around 1303 eV. This positive shift of Mg 1s toward higher binding energies in MgB₂ is related to donating electrons to boron; thereby, leading to stronger bonding in MgB₂ compared to metallic Mg. Besides, in MgB₂, there is a probability of some reverse charge transfer from B to Mg (+2) leading to a diminution of the formal charge of Mg and hence the partial covalency in the Mg-B bond. This charge transfer results in the fragmentary covalency in the Mg-B bond. As written above, in MgB₂ structure—an example of a boron-rich system—the electrons transfer from Mg to B layers.[89] The electrons move to B π -bands

as the σ -bands are filled, Then, some electrons shift from B π to Mg (+2). Consequently, the charge state of Mg is reduced from (+2) to lower states.[103]

A general trend can be observed in Figure 3. 4 and Figure A2 that doping shifts Mg 1s toward higher binding energies. Specifically, in the low doping amount of Co and Fe ($x = 0.025$), Mg 1s peak shifts to even higher peaks, 1305.5 eV (refer to Figure A2). There are differences of > 1 eV in binding energies between doped and undoped samples. These large differences are ascribed to the effect of neighboring atoms. As stated by [110], non-exchangeable and exchangeable Mg ions exhibit peaks around 1303 and 1306 eV, respectively. In low amounts of Co and Fe dopant ($x = 0.025$), Mg ions act as exchangeable ions, whereas, in higher contents of Co and Fe ($x = 0.05$ and 0.1), Mg ions are considered as non-exchangeable ones. For this case, the flow of electronic charge to Mg ion, and the extra-atomic relaxation from surrounding oxygen atoms are larger.

Figure 3. 4 and Figure A2 depict the examined B 1s spectra. B 1s spectra of pure MgB₂ display peaks around 185.2, 186.4, 188.8, and 191.3 pertaining to B(OX), MgB₂ (boron as boride anion), B as metallic, and B₂O₃, respectively. These are consistent with the binding energy values reported for Mg diboride.[103] MgB₂ is viewed as Mg²⁺(B₂)²⁻ with an average charge of (-1) at B. As it was mentioned previously, in the MgB₂ structure, the Mg charge is less than (+2), so the average charge on B is less than (-1). Doping of MgB₂ with metallic elements such as Co and Fe shifts binding energies of B to higher values, especially in the low amount of dopant as $x = 0.025$. This slight increase of binding energy stipulates the partial electron transfer from B to the vacant d-orbital of the metallic dopant.

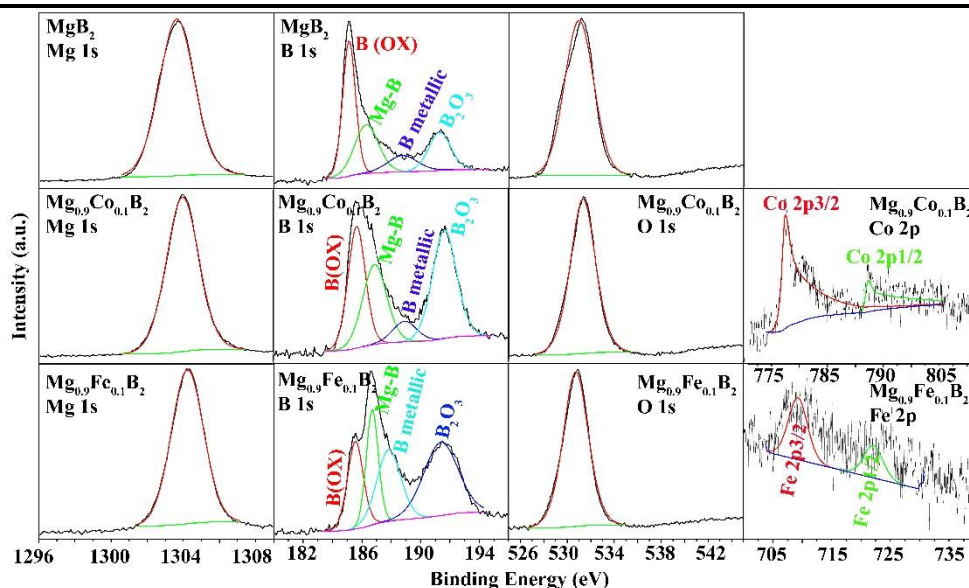


Figure 3. 4. XPS spectra of Mg 1s, B 1s, O 1s, Co 2p, and Fe 2p in MgB₂, Mg_{0.9}Co_{0.1}B₂, and Mg_{0.9}Fe_{0.1}B₂.

To investigate the oxygen-containing compounds at the surface, the O 1s spectra have also been illustrated Figure 3. 4 and Figure A2. The prominent peak around 531 eV corresponds to MgO and surface oxygen possibility. Finally, Co 2p and Fe 2p peaks were observed in all doped samples, confirming the presence of Co and Fe species in the MgB₂ structure. For Fe-doped Mg_{1-x}Tm_xB₂ ($x = 0.025$), Fe 2p_{3/2} peak is also possible, but it could not be deconvoluted due to its low intensity.

The EDX elemental mapping analyses performed at high magnifications on Mg_{0.95}Co_{0.05}B₂ and Mg_{0.9}Fe_{0.1}B₂ indicate the homogenous distribution of the metal atoms throughout the grains of the target phases (Figure A3). Generally, the particle morphology studied by FESEM images (Figure 3. 5 and Figure A4) disclosed that for pure MgB₂, nanoparticle sizes are in the range of 40–300 nm, Fe-doped MgB₂ 29–500 nm, and Co-doped MgB₂ 39–450 nm. Needless to mention that larger particles with sizes as big as 1–2 micrometers were also detected which can be primarily because of agglomeration. The morphology of resulting particles demonstrated that pure MgB₂ has been mostly dominated by spherical shape particles. Nonetheless, samples with a formal composition of Mg_{1-x}Tm_xB₂ displayed quite distinctive particle shapes (e.g., needle-like) that can be ascribed to interaction between metallic and boron layers as well as high pressure applied during their synthesis procedure. Comparing the individual crystallite of Fe and Co substituted MgB₂ signifies the fact that Co-doped samples have slightly better incorporation of Co into the MgB₂ structure. On the contrary, Fe-doped samples lack this

benefit, most probably due to the formation of secondary phases such as FeB or Fe_2B . The mentioned conclusions were also witnessed in ref.[111].

According to the previous literature,[5, 87, 112] catalysts with attributes such as large specific surface area, open porous structure, and high accessibility of active sites are expected to exhibit outstanding electrocatalytic performance. Thanks to the FESEM image of the surface of the working electrode (Figure 3. 6), uneven morphology, pores, and cracks can be observed that facilitates the accessibility of the electrolyte molecules into the far deeper parts of the electrode: thereby, drawing on remarkable catalytic activity.

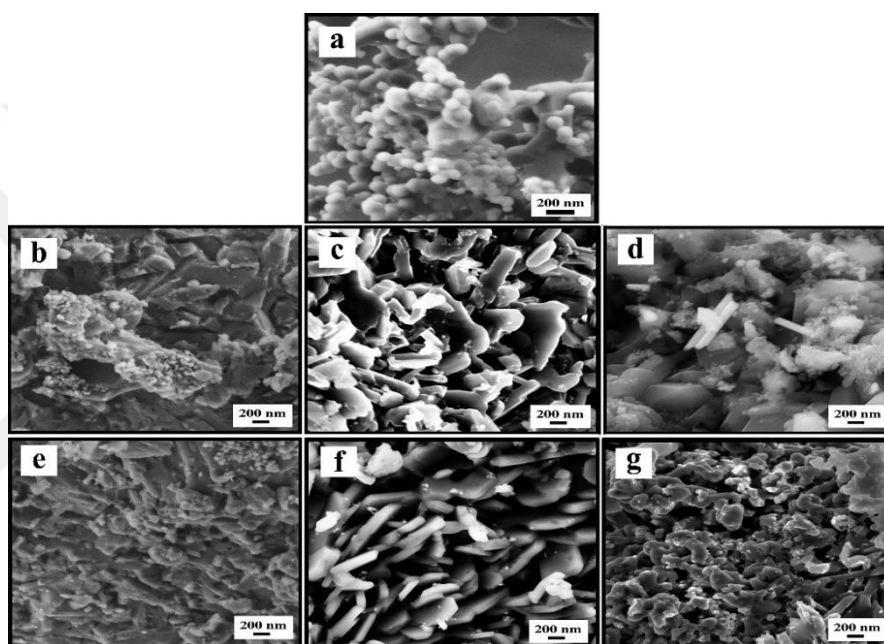


Figure 3. 5. SEM images of a) pure MgB_2 , b) $\text{Mg}_{0.975}\text{Co}_{0.025}\text{B}_2$, c) $\text{Mg}_{0.95}\text{Co}_{0.05}\text{B}_2$, d) $\text{Mg}_{0.9}\text{Co}_{0.1}\text{B}_2$, e) $\text{Mg}_{0.975}\text{Fe}_{0.025}\text{B}_2$, f) $\text{Mg}_{0.95}\text{Fe}_{0.05}\text{B}_2$, and g) $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{B}_2$.

Electrocatalytic features of undoped MgB_2 and transition metal doped MgB_2 were evaluated using electrochemical tests. Both HER and OER were examined carefully. The recorded voltammograms of the OER are given in Figure 3. 7. As is noticeable from this figure, $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{B}_2$ exhibits the superior reactivity amongst all the doped MgB_2 samples. This decent performance should be assigned to the incorporation of Fe atoms into the MgB_2 structure. In addition, as reported by Li et al. on boride-based electrodes, Fe dopants can enhance the local electronic structure owing to its superconductivity, resulting in enhanced OER performance.

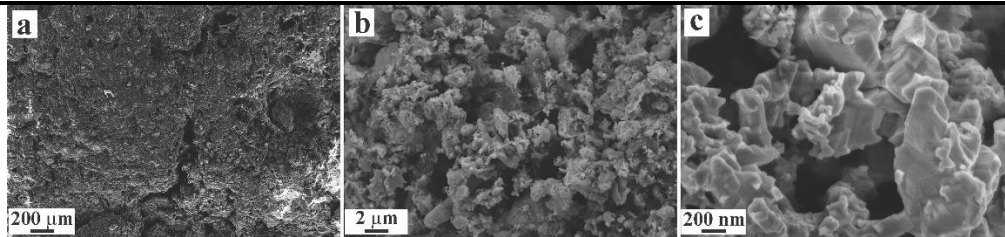


Figure 3. 6. SEM images of the working electrode surface.

The voltammograms of the HER polarization curves are depicted in Figure 3. 8a. For this, LSV electrochemical tests were recorded over a range of potential from -0.2 to -1.6 V vs RHE under the basic 1 M KOH medium. It is striking that doping of MgB₂ with divalent metals affects the HER reaction significantly, as in doped electrodes, the overpotential is extremely lower at -10 mA cm⁻² current density compared to that of pure MgB₂ (see Figure 3. 8a). In this regard, Mg_{0.95}Co_{0.05}B₂ showed the best results in terms of the HER performance with the lowest overpotential at -10 mA cm⁻² current density. This suggests that the HER reaction over Mg_{0.95}Co_{0.05}B₂ proceeds in an efficient manner which is in accordance with the literature—in that—Co-based borides are favorable catalysts in the water reduction reactions.[5]

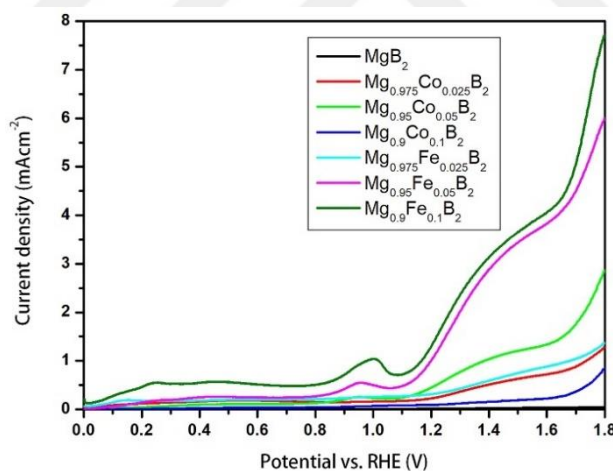


Figure 3. 7. Polarization curves of the OER reaction of pure and doped MgB₂.

As reported by Rafieazad et al., the presence of MgO impurity can impede the connection between the grains and thereby, undermine the superconductivity of MgB₂. Moreover, it has been emphasized that coverage of MgB₂ grains by the MgO layer can diminish the critical current density considerably. With these in mind, Mg_{0.95}Co_{0.05}B₂ and Mg_{0.9}Fe_{0.1}B₂ displayed the highest HER performance respectively on account of the least amount of impurity in terms of MgO (refer to Figure 3. 2).[96]

As it was mentioned previously, TMBs possess remarkable features such as reverse electron transfer from boron to metals resulting in fast electrochemical reactions, surface oxidation of TMBs on the account of the formation of active chemicals such borates, boron oxides, TM oxides, TM (oxy)hydroxides leading to effective catalytic reactions, and heat-treatment of TMBs that can promote catalytic performance as a result of phase change.[4] In addition to these aspects, the effect of hetero-metal doping on TMBs has also been widely reviewed. In this context, it was found that metal doping can expand the specific surface area (SSA) through inhibition of the agglomeration that reflects in the exposure of more available active sites, engineering the crystal structures, and tuning the electronic structures.[4, 113]

It was established that in boride-rich compounds such as FeB₂, Fe as cation holds a partial positive charge, and B as anion carries a partial negative charge. Here, electron transfer from Fe to B expedites the adsorption of OH⁻ on positively charged Fe sites and H⁺ on negatively charged B sites. Regarding MgB₂ as parent electrocatalyst utilized in this study, Fe and Co dopants—more electronegative compared to Mg—have changed surface morphology of the samples, regulated electronic structures, and induced higher electron density transferred from cation site to anion, facilitating both HER and OER reactions.

For better interpretation, EIS analyses were performed in open circuit potential to predict charge transfer resistance through the electrodes. Figure 3. 8b,c presents the Nyquist plots of all the electrodes in full and zoom screen, respectively. As revealed by FESEM images from the electrode surface (Figure 3. 6), the fabricated electrodes possess high porosity. To this end, the impedances were modeled using a so-called constant phase element (CPE) model, (R1-CPE) and (R2-CPE), composed of a solution resistance and a connection between two paralleled R-CPE elements in series—the high-frequency R-CPE element is correlated with the porosity whereas the low-frequency element is related to the kinetics of the HER.

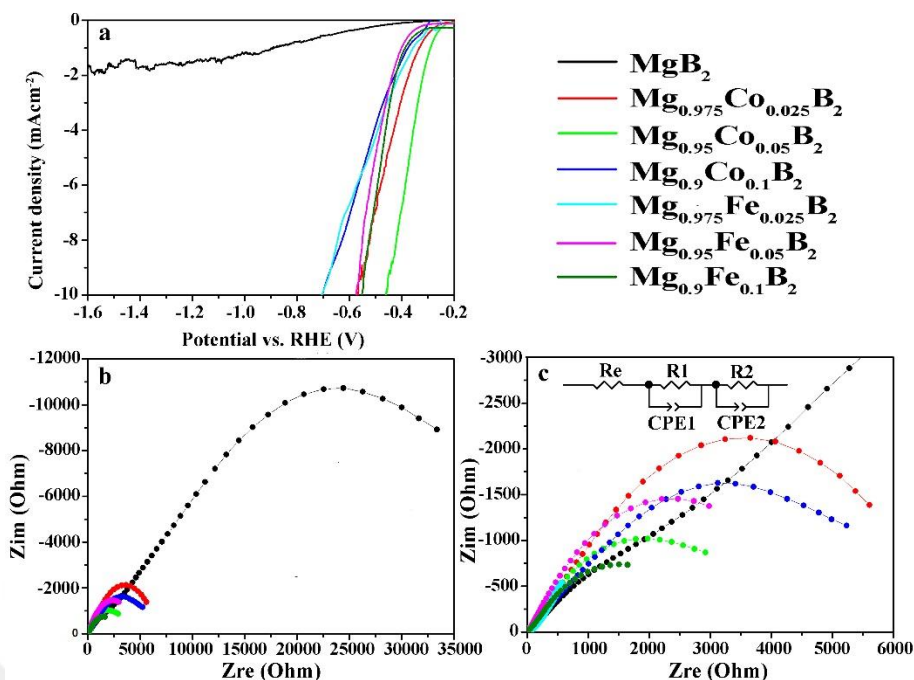


Figure 3. 8. Polarization curves of a) the HER reaction of pure and doped MgB₂, b) and c) Nyquist plots measured at OCP in supporting electrolyte of 1 M KOH.

In principle, the formation of two semicircles on the Nyquist plot corresponds to the geometric kinetic origin. The first semicircle is related to geometric and the second one is related to kinetic. The diameter of the semicircles represents the charge transfer resistance. Both the transfer of electronic charge on the electrode/electrolyte interface and the charge transfer in the host lattice control the electrochemical reactions at the electrodes. The acquired results for the Nyquist equation by Z-view software are summarized in Table 3.2 (detailed data in Table A3). The results support that metal doping of MgB₂ has dramatically decreased both R1 (charge-transfer resistance of the electrode/electrolyte interface) and R2 (charge-transfer resistance of the host lattice), and therefore increased the electrochemical catalytic activity.

As Mg is a highly reactive metal, it can readily get oxidized and converted into Mg(OH)₂ on the electrode surface in the KOH solution. The very plain interpretation would be, the formation of Mg(OH)₂ on the surface can block available active sites, increase the reaction resistance and restrain the diffusion of H atoms into the inner phase. Taking this interpretation into account, the high value of R1 (10.993 kΩ cm⁻²) in undoped MgB₂ explains itself. On the contrary, the substitution of Co²⁺ and Fe²⁺ for Mg²⁺ in the alloy reduces the formation of Mg(OH)₂ and improves the life cycle of the electrode. Additionally, doping amplifies the electron mobility and conductivity of the electrodes,

yielding much lower amounts of R₂ for the doped electrocatalysts (see Table 3.2). Overall, Mg_{0.9}Fe_{0.1}B₂ (7.980 kΩ cm⁻²) and Mg_{0.95}Co_{0.05}B₂ (10.409 kΩ cm⁻²) have the lowest charge-transfer resistance in terms of R₂ among the doped electrodes; as a result, they outperform all others in the sense of electrocatalytic performance.

Table 3. 2. Equivalent-circuit element values for EIS data in the 1 M KOH electrolyte.

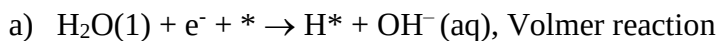
Sample	Re (Ωcm ⁻²)	R1 (kΩ cm ⁻²)	R2 (kΩ cm ⁻²)
MgB ₂	130.5	10.993	127.114
Mg _{0.975} Co _{0.025} B ₂	12.2	1.436	18.331
Mg _{0.95} Co _{0.05} B ₂	13.6	0.409	10.409
Mg _{0.9} Co _{0.1} B ₂	13.2	3.539	13.712
Mg _{0.975} Fe _{0.025} B ₂	7.52	0.454	710
Mg _{0.95} Fe _{0.05} B ₂	13.5	0.277	14.325
Mg _{0.9} Fe _{0.1} B ₂	11.9	0.332	7.980

To assess the probable degradation of the electrocatalysts after electrochemical reactions, FESEM coupled with EDX analyses were conducted on the samples. Figure A5 presents the EDX results of the samples after electrochemical reactions at different spots and the outcomes have been reported with and without oxygen content. Based on semi-quantitative analysis results in Tables A1 and A4, it can be observed that there are slight changes in the atomic percent of all elements after HER and OER, implying that the fabricated electrodes have remained largely intact. Considering that reactions have taken place in 1 M KOH, increasing the atomic percent of oxygen on the surface of both best-performing electrodes from 3.63 to 10.59 % and 3.12 to 14.93 % corresponding to Mg_{0.95}Co_{0.05}B₂ and Mg_{0.9}Fe_{0.1}B₂ is not surprising. It is assumed that the surface metal hydroxide/oxyhydroxide produced in the course of OER is the major ground for the high water oxidation performance. As a result, high oxygen contents for the post-OER electrodes can be ascribed to Mg-, Fe-, and Co- hydroxide/oxyhydroxide. In addition to this, higher alterations in the atomic percent of metals—Mg, Fe, and Co—can be witnessed compared to nonmetal B. For the case of Mg, it should be noted that inevitably unreacted Mg before HER and OER reactions have been consumed as Mg-hydroxide/oxyhydroxide leading to less Mg contents after electrochemical reactions for both electrodes.

For the practical applications in the electrocatalytic process, overpotential should be kept to the lowest amounts to deliver a benchmark current density of 10 mA cm⁻² during the process. For this reason, metal doping is not only an efficient way to improve the sluggish kinetics of HER but also is beneficial to lower the kinetic energy resistances of electrocatalytic reactions. The overpotentials of Co- and Fe-doped MgB₂ at -10 mA cm⁻² are shown in Figure 3. 9a indicating the HER performance of the electrodes. Mg_{0.95}Co_{0.05}B₂ has a low overpotential of 470 mV at -10 mA cm⁻² amidst all the investigated samples owing to its high purity. However, the other Co-doped electrodes did not follow any specific activity trend. In contrast, the activity trend in Fe-doped electrodes showed an inverse relation with Fe content. By increasing Fe amount, overpotential diminished, giving rise to the following trend Mg_{0.9}Fe_{0.1}B₂ < Mg_{0.95}Fe_{0.05}B₂ < Mg_{0.975}Fe_{0.025}B₂.

Concerning the fact that there has been a limited number of reports on layered MDbs in HER, a brief comparison of overpotentials with the present work and recently reported boride based electrocatalysts would be intriguing. For this, Mazánek et al.[114] stated HER performance of several layered MDbs including MgB₂ in 0.5 M H₂SO₄. According to this report, the best performing MDb was ZrB₂ with an overpotential of over 950 mV at a current density of -10 mA cm⁻². Moreover, an elaborate review was recently published by Gupta et al.[2] Here, a few results on overpotential of metal borides in 1 M KOH solution are given: Mo-B ≈ 240 mV (20 mA cm⁻²), NiB_x film ≈ 135 mV (10 mA cm⁻²), Ni-B ≈ 125 mV (20 mA cm⁻²), Co₂B-CoSe₂ ≈ 300 mV (10 mA cm⁻²), Co-Ni-B ≈ 205 mV (10 mA cm⁻²), and FeB₂ ≈ 61 mV (10 mA cm⁻²). Even though at first glance the investigated electrocatalysts in this study appear less competent compared to the above-written non-precious electrocatalysts, it should be overemphasized that the present results emerged with trace amounts of dopants and economical precursors, showing a great promise for future works.

Figure 3. 9b presents Tafel curves for all the synthesized electrodes. The Tafel slope is a crucial indication of reaction kinetics and rate in the HER process.[115] In other words, it is an intrinsic factor for the assessment of the rate-determining steps in the course of HER.[116] According to the previous studies,[116, 117] two general paths are proposed for hydrogen evolution in alkaline solutions; either based on Volmer–Heyrovsky mechanism (a and b) or the Volmer-Tafel mechanism (c and d):



- b) $H^* + H_2O(1) + e^- \rightarrow H_2(g) + OH^-(aq) + *$, Heyrovsky reaction
- c) $H_2O(1) + e^- + * \rightarrow H^* + OH^-(aq)$, Volmer reaction
- d) $H^* + H^* \rightarrow H_2(g) + 2*$, Tafel reaction

In the foregoing reactions, * represents available active sites and H* hydrogen atoms bound to active sites. Moreover, it has been estimated that the required Tafel slopes for Volmer reaction, Heyrovsky reaction, and Tafel reaction are $\sim 120 \text{ mV dec}^{-1}$, $\sim 40 \text{ mV dec}^{-1}$, and $\sim 30 \text{ mV dec}^{-1}$, respectively,[118] Regarding the Tafel slopes shown in Figure 3. 9b, Mg_{0.95}Co_{0.05}B₂ has the smallest Tafel slope, 80 mV dec⁻¹ which indicates that it falls within the range of 40-120 mV dec⁻¹, demonstrating the Volmer-Heyrovsky mechanism. This superior performance accords with overpotential results as well, suggesting facile kinetics and faster electron transport on Mg_{0.95}Co_{0.05}B₂ as compared to all other samples. Interestingly, Mg_{0.975}Co_{0.025}B₂ with a Tafel slope of 112 mV dec⁻¹, Mg_{0.95}Fe_{0.05}B₂ with that of 117 mV dec⁻¹, and Mg_{0.9}Fe_{0.1}B₂ with a slope of 131 mV dec⁻¹ have relatively comparable catalytic activity, proceeding via Volmer mechanism. Other doped samples that displayed rather higher Tafel slopes likely suffered from insufficient conductivity and low accessible active sites.[116, 117, 119]

Despite the fact that too high the Tafel slope necessitates the electrocatalyst to provide excessive overpotential to meet the required current density,[117] we cannot draw a clear conclusion based on the relation between overpotential and Tafel slope. Nonetheless, a meaningful point is revealed—that is—at low overpotential (Mg_{0.95}Co_{0.05}B₂, Figure 3. 9a) the Volmer–Heyrovsky reaction is dominated, while at high overpotential (Fe-doped samples, Figure 3. 9a) the Volmer–Tafel reaction prevails. The preceding remark is substantiated by the literature as well.[120]

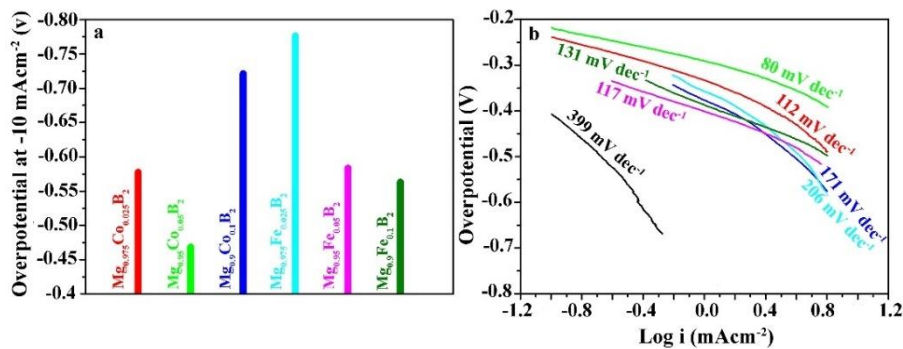


Figure 3. 9. Fundamental electrochemical properties for HER. a) Overpotential at -10 mA cm^{-2} of metal-doped MgB₂, b) The corresponding Tafel plots of undoped and doped MgB₂. The colors indicating the same samples pictured in Figure 3. 8.

The stability tests of the Mg_{0.95}Co_{0.05}B₂ and Mg_{0.9}Fe_{0.1}B₂ electrodes were performed by the cyclic voltammetry (CV) scanning method. Specifically, the current density was measured over a scanning rate of 50 mV s⁻¹ in a voltage window of -1 V to -0.2 V vs RHE for HER under 1 M KOH solution. (see Figure A6). Altogether, for HER stability tests, even though the current density did not decrease appreciably, further investigations are needed to excel in the stability of these very new electrocatalysts.

3.4.CONCLUSIONS

In this work, we performed a straightforward scalable method to synthesize a series of novel metal-doped MgB₂ with earth-abundant elements, Fe and Co, with a loading concentration of 0.025, 0.05, and 0.1. The as-prepared materials anchored on a copper foil were employed as electrodes for the water-splitting process to function as HER electrocatalysts. Meanwhile, they were examined as OER catalysts as well. The overall outcomes substantiated that introduction of Co and Fe into the structure of layered MgB₂ meaningfully enhanced both OER and HER performance. In this way, a remarkable improvement of OER activity for Fe-doped MgB₂ electrodes was ascribed to the dramatic reduction of charge-transfer resistance both at electrode/electrolyte surface and within the host lattice. As a result, increasing Fe content gave rise to outstanding OER activity corresponding to Mg_{0.9}Fe_{0.1}B₂, by virtue of its optimum values of charge-transfer resistance. Besides, the best-performing catalyst in terms of HER was obtained for Mg_{0.95}Co_{0.05}B₂ displaying an overpotential of 470 mV at -10 mA cm⁻² and a small Tafel slope of 80 mV dec⁻¹. This notable performance arose from several factors including the efficacious integration of Co in the crystal structure, facile kinetics, and fast electron transport that resulted in a drastic abatement of charge-transfer resistance in the host lattice compared to the undoped sample (10.409 vs. 127.114 kΩ cm⁻²). This comprehensive electrochemical study conducted on Fe and Co-doped MgB₂ may provide further insights into designing new earth-abundant and efficient materials that rival and exceed the performance of conventional electrocatalysts.

CHAPTER 4

TAILORING THE MORPHOLOGY OF COST-EFFECTIVE VANADIUM DIBORIDE THROUGH COBALT SUBSTITUTION FOR HIGHLY EFFICIENT ALKALINE WATER OXIDATION



The majority of this chapter has been published in *Inorganic Chemistry*, 2021, 60(24), 19457-19466. The original manuscript has been rearranged to conform to the format requirements of the dissertation.

4.1.Introduction

Lately, our group explored layered MgB_2 and ZrB_2 MDbs as potential materials for both HER and OER.[121, 122] Inspired by encouraging results, we report electrocatalytic features of layered metallic vanadium diboride (VB_2) for OER. VB_2 adopts the hexagonal AlB_2 structure type with the space group $P6/mmm$. [123] As an ultrahigh-temperature ceramic material, VB_2 combines exceptional physical traits such as extraordinary wear and corrosion tolerance as well as decent chemical durability with remarkable electrical conductivity which makes it an inherently competent electrocatalyst for OER.[124-126] Not to mention that the presence of graphene-like B layers sandwiched with V atoms facilitates the electron transfer throughout the whole structure, suggesting that VB_2 is a worthwhile candidate for photo/electrocatalysis.[123, 127]

Thus far, there have been a handful of reports on photo/electrocatalysis of VB_2 namely experimental and theoretical exploration for electrocatalytic HER[128] and examination of its qualities as an efficient cocatalyst for dye-sensitized photocatalytic HER.[129-131] Furthermore, different research groups separately selected a class of MDbs and studied their electrocatalytic activities towards HER, claiming that VB_2 is amidst those that hold attractive features.[9, 114, 132] Keeping these in mind, we present herein the robust and durable $\text{V}_{1-x}\text{Co}_x\text{B}_2$ ($x = 0, 0.05, 0.1$, and 0.2) for OER under 1 M KOH solution. It should be stressed that $\text{V}_{0.9}\text{Co}_{0.1}\text{B}_2$ afforded a very low overpotential of 200 mV which is among the lowest values reported so far. A reasonable comparison with TMBs can easily justify the superb performance of $\text{V}_{0.9}\text{Co}_{0.1}\text{B}_2$. To this end, Nsanzimana *et al.* reported bimetallic iron-nickel boride (Fe-Ni-B) ultrathin nanosheet on Ni foam (NF) which required 237 mV to reach a current density of 10 mA cm^{-2} . [133] Liu *et al.* presented the amorphous NiFeB nanoparticles with an overpotential of 216 mV on NF and 251 mV on glassy carbon (GC).[134] In another study, Li *et al.* documented that NiFeLDH/NF requires an overpotential of 224 mV to deliver a current density of 10 mA cm^{-2} . [135] Even though the mentioned studies and many others exploited different substrates such as NF—intrinsically active material—the as-prepared electrocatalysts in this work on GC surpass them in terms of oxygen-evolving reaction. We do believe that this is the first time the electrocatalytic characteristics of VB_2 and its derivatives for OER have been probed.

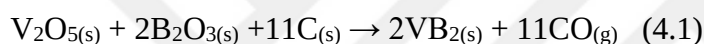
4.2. EXPERIMENTAL SECTION

4.2.1. Chemical Reagents

Vanadium pentoxide powder (V_2O_5 , Sigma Aldrich, 99.95% trace metals basis), boron oxide powder (B_2O_3 , Alfa Aesar, 99%, metals basis), activated charcoal powder (C, Sigma Aldrich, pure), and cobalt powder (Co, Sigma Aldrich, 99.99% trace metals basis).

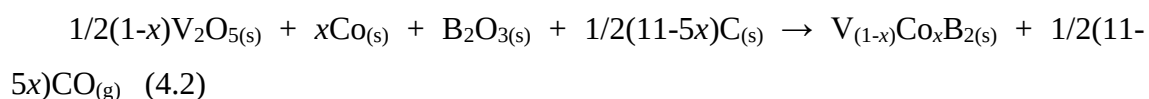
4.2.2. Synthesis of Electrocatalysts

In this study, parent VB_2 and Co-substituted VB_2 were prepared at 1723 K by a carbothermal reduction method. Stoichiometric amounts of reactants V_2O_5 , B_2O_3 , and C were weighed according to the theoretical reduction reaction given in Equation 4.1 for the formation of parent vanadium diboride powder.



The weighing and transferring of starting materials into a hardened stainless-steel vial were carried out under a protected atmosphere (Ar) in a glovebox (MBraun Labmaster Pro DP) (O_2 and H_2O level < 0.1 ppm). Before heat treatment, the solid mixture of powders was mechanically activated by using high-energy ball milling (Spex™ 8000D Mixer/Mill) for 180 min with 1400 rpm. Milling was performed with a ball to powder weight ratio of 13:1 using steel balls of two 1/2" and four 1/4" in diameter. Thereafter, the resulting powder was undergone heat treatment using graphite crucible in a sealed tube furnace. The solid mixture was heated from room temperature to 1723 K with a heating rate of 10 K/min and kept at that temperature for 360 min under constant Ar flow to restrain oxidation.

For the substitution experiments given in Equation 4.2 cobalt powder was used with different loadings ($x = 0.05, 0.1, \text{ and } 0.2$). The remaining steps were followed according to the above-written recipe.



4.2.3. Electrode Fabrication

The catalysts inks were made by thoroughly mixing 2 mg of VB₂ powders in a 480 μ L pure ethanol-deionized (DI) water mixture (380:100) under ultrasonication for 20 min, followed by the addition of 5% wt Nafion solution (5 μ L) to the mentioned mixture, accompanied by another 20 min of ultrasonication to achieve a homogeneous catalyst slurry. 10 μ L of the catalyst ink was pipetted out on the pre-treated surface of GC. Finally, the catalyst-coated surface of the GC electrode was dried under an air atmosphere at 80 $^{\circ}$ C for 120 min. A similar process was adopted to fabricate the commercial RuO₂ electrode. All electrodes were constructed with a loading of $\sim$ 0.5 mg/cm².

4.2.4. Characterizations

Powder XRD patterns were measured on Rigaku Mini Flex 600; Cu K α (λ = 1.5418 Å) diffractometer equipment. The XRD spectra were recorded over an angular range of 20 $^{\circ}$ to 90 $^{\circ}$. It should be highlighted that a zero-background powder specimen holder was utilized for the XRD analysis of all samples. To characterize the surface morphology and chemical composition, Zeiss Ultra Plus FESEM was used at a maximum accelerating voltage of 15 kV for Energy Dispersive X-ray Spectroscopy (EDS). Additional characterizations on morphology and microstructure of the samples were carried out by transmission electron microscopy (TEM) using a Hitachi HT7700 TEM instrument operating with a maximum acceleration voltage of 120 kV. To further understand the electronic configuration of prepared samples XPS was performed by using a Thermo Scientific K-Alpha X-Ray Photoelectron Spectrometer system equipped with an AlK α microfocused monochromator source (1486.6 eV) operating at 400 mm spot size and accompanied by a flood gun for charge neutralization. The selected area electron diffraction (SAED) images were collected with a Hitachi HF5000 200kV aberration-corrected TEM.

4.2.5. Electrochemical Measurements

To evaluate the electrochemical characteristics of the prepared electrocatalysts, we followed a similar strategy to our earlier report.[122] Succinctly, the electrochemical tests were performed on an AutoLab Potentiostat Galvanostat (PGSTAT302N, made in the Netherlands) using a three-electrode cell equipped with standard Reversible Hydrogen

Electrode (RHE; HydroFlex) as reference electrode and Pt wire as a counter electrode under 1 M KOH medium. A 3 mm-diameter GC was employed as a working electrode, polished with diamond suspension (MetPrep, 1 micron) and treated with distilled water and ethanol each for 10 min prior to each run. To this end, the LSV curves were recorded from +1.2 to +1.8 V vs. RHE towards OER at a sweep rate of 5 mV s^{-1} . The required overpotential for water oxidation was calculated at a current density of 10 mA cm^{-2} . In addition, the longevity of the prepared electrocatalysts was determined by chronopotentiometry at 10 mA cm^{-2} for 12 h. The CV operations were carried out at a sweep rate of 5 mV s^{-1} . Furthermore, a frequency ranging from 100 kHz and 0.1 Hz with a 10 mV RMS sinusoidal modulation at 0 V was considered to obtain the electrochemical impedance spectroscopy (EIS) curves.

Finally, the Faradaic efficiency (FE) of O_2 production by the selected electrocatalyst was measured by the Bipotentiostat using a Rotating Ring-Disk Electrode (RRDE) set-up (Pine Research Instrumentation, Durham, NC) where GC and Pt were used as disk and ring electrodes, respectively. The collection efficiency, N , of the RRDE assembly, was independently established to be $N = 0.84$ from consecutive reduction and oxidation of $\text{K}_3\text{Fe}(\text{CN})_6$ at a GC electrode and the Pt ring, separately (Figure B1). RRDE measurements were conducted in a cell purged with N_2 for ~ 30 min prior to each run to maintain the N_2 -blanket during the experiment. A rotation rate of 1600 rpm was used for RRDE measurements in N_2 -saturated 1.0 M KOH. The target catalyst was drop cast onto the interchangeable GC disk electrode. Before measurement, the Pt ring was polished with an alumina slurry, then washed and sonicated in DI water. The disk electrode containing the electrocatalyst was held at the open circuit potential of OER for 60 s where no Faradaic process occurs, while the Pt ring electrode was maintained at 0.2 V vs. RHE to establish the background current of the ring electrode. The background ring current was lower than 50 μA . Thereafter, the potential of the disk electrode was kept at certain values in the OER kinetic region in N_2 -saturated 1.0 M KOH for 60 s while the ring current was recorded at 0.2 V vs. RHE.

4.3.RESULTS AND DISCUSSION

4.3.1. Chemical Studies

Figure 4. 1 illustrates the XRD pattern of pristine VB_2 , verifying its successful synthesis. The characteristic peaks positioned at 29.19° , 34.53° , 45.82° , 60.53° , 61.84° , 69.83° , 71.60° and 72.81° can be indexed to the respective crystal planes of hexagonal phase VB_2 (001), (100), (101), (002), (110), (111), (102), and (200) (JCPDS 38-1436) that are very well-matched with the literature.[129, 130] No impurity peaks—secondary phases—were detected for pristine VB_2 . Concerning Co-substituted VB_2 samples, impurity-phase reflections are more pronounced with respect to Co content in VB_2 . In this context, $\text{V}_{0.95}\text{Co}_{0.05}\text{B}_2$ contains a trace amount of impurities. On the contrary, the XRD pattern of $\text{V}_{0.8}\text{Co}_{0.2}\text{B}_2$ implies the formation of secondary phases at 29.7° , 36.2° , 39.74° , and 45.5° pertaining to CoVB_3 (marked by #) as well as peaks at 41.3° and 45.5° with very low-intensity corresponding to CoB (marked by *).

It should be overemphasized that according to the XRD patterns (Figure 4. 1) the amount of secondary phases such as CoB and CoVB_3 within the matrix of $\text{V}_{0.95}\text{Co}_{0.05}\text{B}_2$ is extremely low. Increasing the amount of Co to $x = 0.1$ in $\text{V}_{0.9}\text{Co}_{0.1}\text{B}_2$ results in minuscule growth of undesired phases. However, the amount of these phases is still not pronounced. Finally, increasing Co content to $x = 0.2$ in $\text{V}_{0.8}\text{Co}_{0.2}\text{B}_2$ leads to the growth of impurity peaks to a noticeable degree, suggesting that substitution over a certain amount of Co ($x = 0.1$), gives rise to secondary phases, which means Co does not go into the structure of VB_2 . Instead, it forms other phases such as CoB and CoVB_3 .

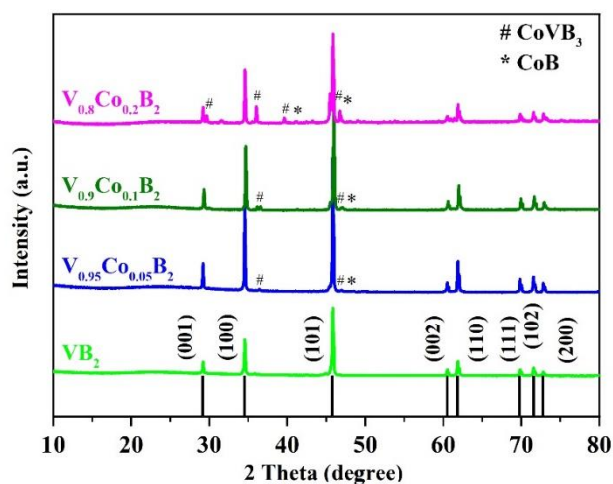


Figure 4. 1. XRD patterns of $\text{V}_{1-x}\text{Co}_x\text{B}_2$ ($x = 0, 0.05, 0.1$, and 0.2).

The particle size and morphology of the as-prepared samples were scrutinized in particular using SEM. From SEM images of unsubstituted VB_2 (Figure 4. 2), it can be seen that plenty of fused spherical particles—regular and smooth—were grown at high temperatures. The size of these aggregated particles exceeds 1 μm . The corresponding EDS mappings confirm that parent VB_2 is predominantly composed of V and B elements. Due to the fact that no oxygen-containing species were detected from XRD patterns, the oxygen content observed in Figure B2 and Table B1 stems from surface oxygen. It should be emphasized that the EDS elemental compositions emanating from Co-incorporated samples match with the nominal compositions (refer to Table B1). From Figure 4. 3, it can be noticed that incorporation of Co into the VB_2 matrix has utterly transformed the morphology—irregular and coarse monolith-like— of the catalysts, leading to the demolition of the aggregated morphology and development of separate particles. It should be noted that the specific surface area (SSA) of a catalyst is in reverse relation to agglomeration, a decrease in the latter brings about an increase in the former.[4] The EDS elemental mappings substantiate that $\text{V}_{0.9}\text{Co}_{0.1}\text{B}_2$ has more uniform dispersion of Co in the framework compared to the other two samples; $\text{V}_{0.95}\text{Co}_{0.05}\text{B}_2$ and $\text{V}_{0.8}\text{Co}_{0.2}\text{B}_2$ (see Figure B3 and Figure B4). In addition, the transmission electron microscopy (TEM) image shown in Figure 4. 4 reveals a selected ultrathin nanosheet with a few nanometer thicknesses from the analyzed sample batch. The SAED was recorded along the $[-101]$ zone axis in which the diffraction spots could be well indexed with the hexagonal crystal structure of VB_2 .

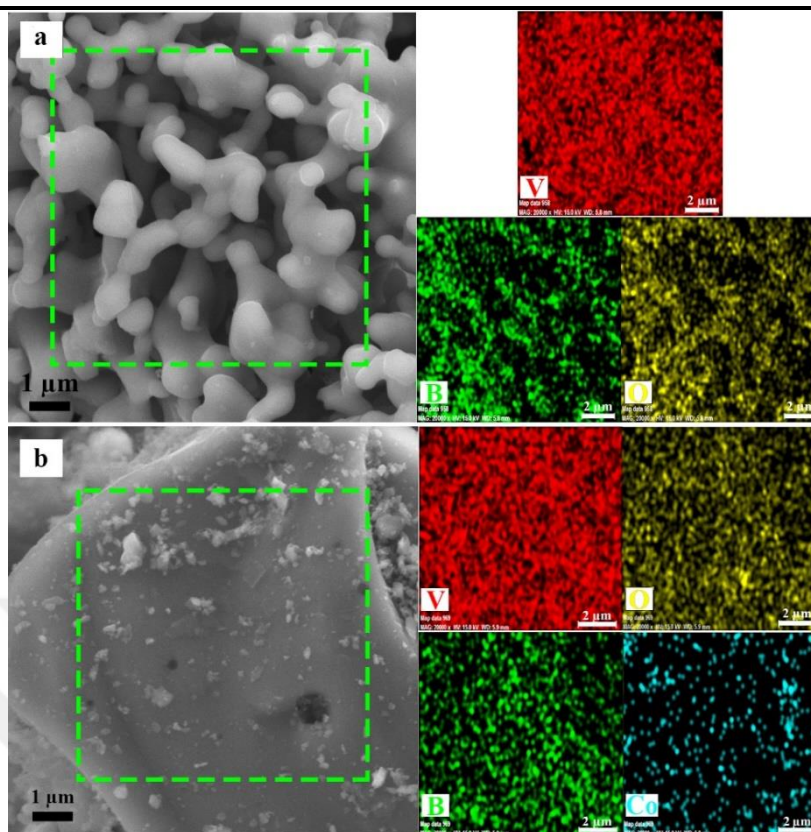


Figure 4. 2. SEM images and corresponding EDS elemental mapping of a) VB_2 and b) $\text{V}_{0.9}\text{Co}_{0.1}\text{B}_2$.

XPS measurement was conducted to further scrutinize the surface composition and electronic configuration of pristine VB_2 and Co-substituted samples. Figure 4. 5 illustrates the fitted spectra of V 2p, B 1s, Co 2p, and O 1s for the best-performing sample ($\text{V}_{0.9}\text{Co}_{0.1}\text{B}_2$). It can be observed that V 2p is classified into two components, V 2p_{1/2} and V 2p_{3/2}, on account of strong spin-orbit coupling of 2p states, each of which has a three-doublet structure.[123] The binding energies (BE) positioned at 512.6 and 520.2 eV (V 2p_{3/2} and V 2p_{1/2} respectively) are assigned to V – B and those located at 516.2 and 524.1 eV (V 2p_{3/2} and V 2p_{1/2} respectively) can be indexed to V – O.[123, 129] It was reported that these doublet peaks are related to V^{3+} , V^{4+} , and V^{5+} ions in the order of increase in BE.[136, 137] In addition, the strong V^{5+} signal suggests that the majority of V oxidation in the $\text{V}_{0.9}\text{Co}_{0.1}\text{B}_2$ arises from +5; nonetheless, the source of V^{4+} is not well defined. Still, with reference to Silversmit *et al.*[138] V^{4+} and V^{5+} can be correlated to VO_2 and V_2O_5 , indicating that the major contribution to the V 2p_{3/2} emanates from V^{5+} . From Figure 4. 5, it can be concluded that weaker BE at 513.6 and 521.8 eV (V^{4+}) can be assigned to VO_2 .

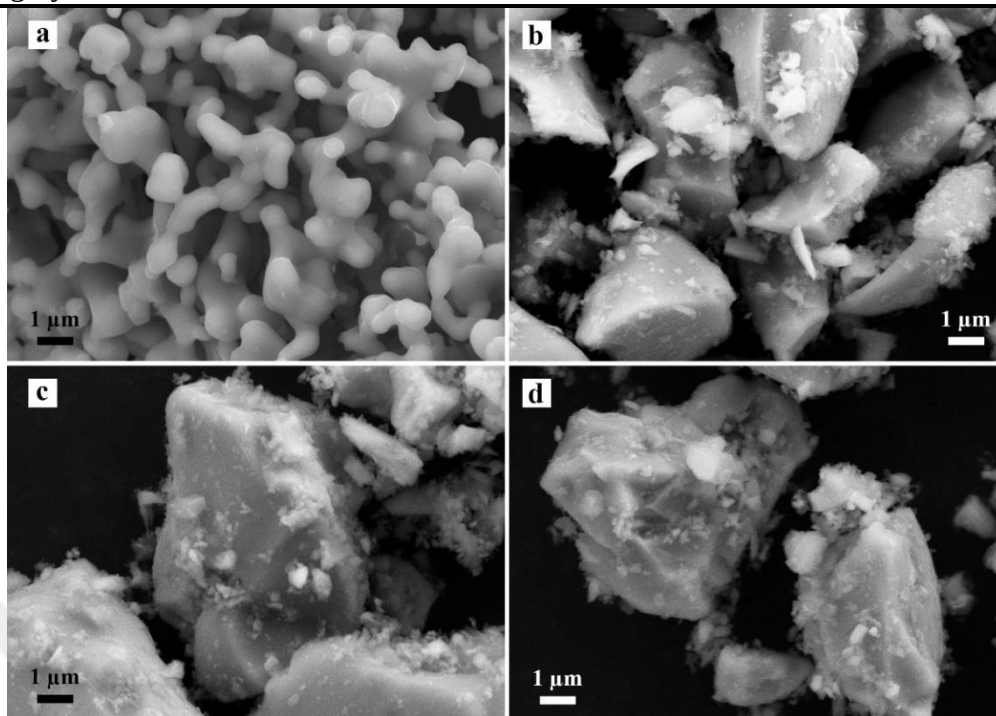


Figure 4. 3. SEM images of a) VB_2 , b) $\text{V}_{0.95}\text{Co}_{0.05}\text{B}_2$, c) $\text{V}_{0.9}\text{Co}_{0.1}\text{B}_2$, and d) $\text{V}_{0.8}\text{Co}_{0.2}\text{B}_2$.

Further, the deconvolution of the B 1s spectrum unveiled peaks at BE of 187.8, 190, and 192.1 eV pertaining to B – V, metallic B, and B – O species, separately.[123, 128, 129] Similar to V 2p, the Co 2p spectrum was divided into two components of Co 2p_{1/2} and Co 2p_{3/2}. The noticeable peaks at 778 and 793 eV are expected ones for elemental Co⁰ in cobalt borides.[139] The other pair located at 782.1 and 798 eV are correlated with Co²⁺ which might be a hint of the existence of CoO or Co(OH)₂. [139, 140] It is worth mentioning that two shake-up satellite peaks (787.1 and 803.3 eV) are representative spin-orbit peaks of Co²⁺. [136] Finally, the O 1s region of the XPS spectrum (also see Figure B5) was likewise scrutinized to specify the two peaks related to O species. For this, the O 1s peak at around 530.5 eV can be appertained to metal (V, B, or Co)-oxygen bonds[141, 142], and the one located at 532.2 eV can be correlated with surface oxygen (adsorbed water or hydroxyl groups).[136]

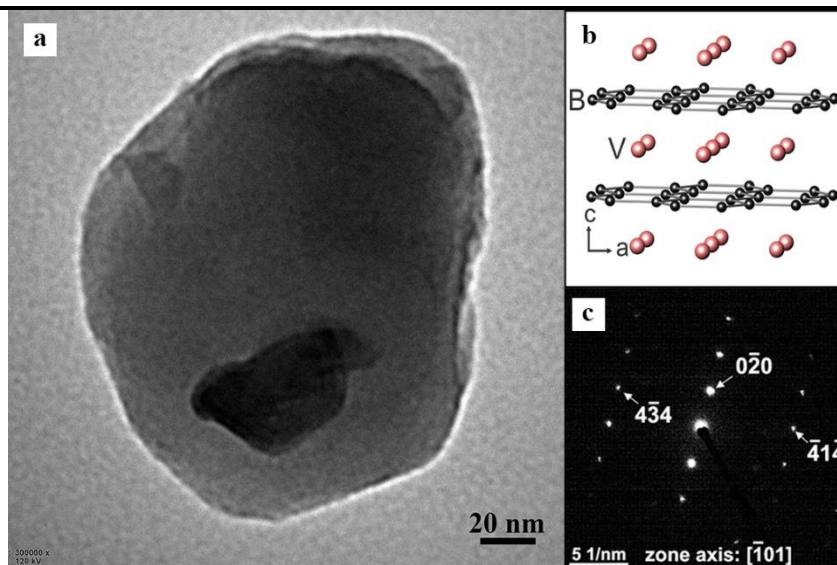


Figure 4. 4. a) TEM image of $V_{0.9}Co_{0.1}B_2$, b) Crystal structure of VB_2 , and c) SAED pattern of $V_{0.9}Co_{0.1}B_2$.

4.3.2. Electrochemical Studies

As depicted in Figure 4. 6a, we can readily distinguish the tremendous impact of Co substitution on the cation sites of VB_2 . The benchmarking OER catalyst, commercial RuO_2 , can also be observed in this figure. The overpotential (at yardstick 10 mA cm^{-2}) of as-prepared catalysts together with RuO_2 follow such a trend $V_{0.9}Co_{0.1}B_2$ (200 mV) < $V_{0.8}Co_{0.2}B_2$ (270 mV) < RuO_2 (290 mV) < $V_{0.95}Co_{0.05}B_2$ (390 mV) < VB_2 (410 mV). The striking result emerging from a moderate amount of substitution of Co ($x = 0.1$) into bare VB_2 stands out in terms of OER performance and exceeds that of RuO_2 . In addition, this finding is to a large extent comparable to other quintessential boride-based electrocatalysts such as Co_1-Fe_1-B-P nanochains ($225 \text{ mV at } 10 \text{ mA cm}^{-2}$)[143] and $Co-B/Ni$ ($140 \text{ mV at } 10 \text{ mA cm}^{-2}$) (refer to introduction section for more details).[144] Comparing the huge difference between the afforded overpotential of unsubstituted VB_2 with that of $V_{0.9}Co_{0.1}B_2$ indicates the profound significance of not only Co within the structure but also the synergistic effect between metals (Co and V) and metalloid (B).

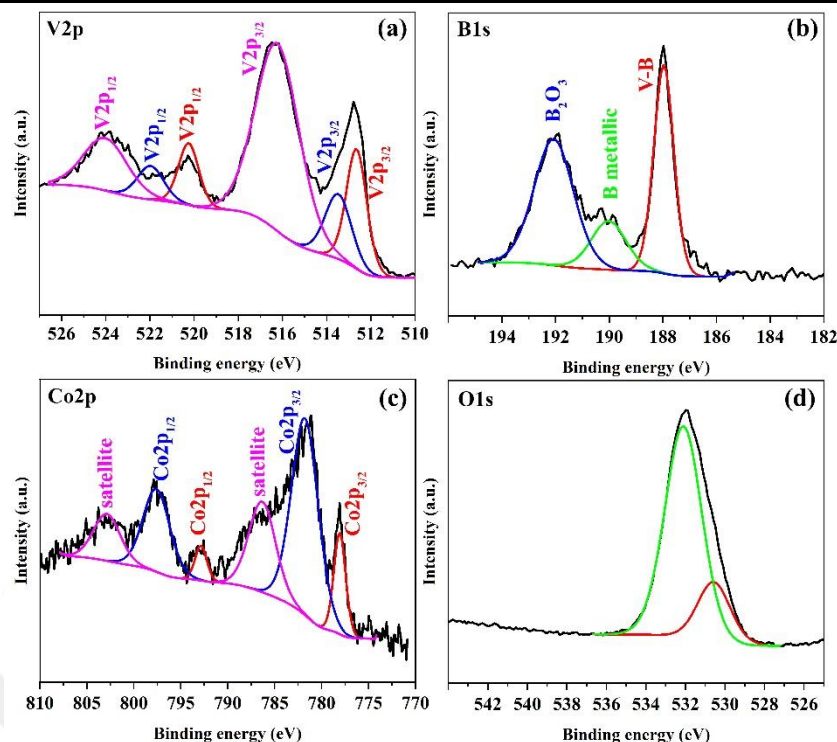


Figure 4. 5. High-resolution XPS spectrum of a) V 2p, b) B 1s, c) Co 2p, and d) O 1s for $V_{0.9}Co_{0.1}B_2$.

It is generally believed that the catalytic performance of a catalyst inclusive of metal-metalloid elements—V and B in this work—can be modulated and in turn strengthened via introducing more metal elements.[145, 146] The facilitated charge transfer between multiple elements tunes the electronic structure, regulates the absorption energy of the intermediates such as OH^* during water oxidation, and consequently alleviates the kinetic energy barriers.[113, 147] It should be pointed out that the catalytic capacity of a target material is subject to several parameters including the electronic structure, the particle size and morphology, and the distribution of active sites. Amidst those, however, manipulation of electronic structure is a game-changing factor, owing to its accompanying critical aspects such as the electronic states, band structures, and adsorption ability. To address this concern, elemental doping has been proposed as a practical tool to fine-tune the electronic structure, and thereby improve wettability properties, alleviate the kinetic energy barrier, and introduce additional active sites. [148]

Substitution of one or more metal atoms into the structure of a host framework (e.g. Ni_2P) has been witnessed to favorably alter the catalytic ability.[149-151] For instance, Co substitution was shown to improve the OER performance of Ni_2P . [151] In another study, Fe introduction into the structure of Ni_2P regulated the adsorption and desorption energies of oxygen-bearing intermediates on an amorphous surface.[150] The catalytic

capacity of Ni₂P was ascribed to the shrinkage of the *d*-band.[152] In other words, the unsatisfactory water oxidation activities mean that the central moment of the *d*-band (*d*-band center relative to the Fermi level (E_F)) of Ni₂P is far from the OER level. Therefore, by reducing the energy level of the *d*-band center (E_d), the oxygen-bearing intermediates are less strongly bound to the Ni₂P surface, because more electrons will fill the antibonding states and be occupied when adsorption takes place between the TM and adsorbates.[153]

Sun *et al.*[154] performed density functional theory (DFT) calculations to further explore the role of Fe incorporation into the host material Ni₂P and its impact on OER activity. They found that the non-uniform distribution of charge can be amplified via Fe substitution and thus increase the density of states (DOS) near the E_F energy level, resulting in increasing the E_d energy level of (Ni_{*x*}Fe_{1-*x*})₂P. Additional theoretical characterizations revealed that the E_d energy level of (Ni_{*x*}Fe_{1-*x*})₂P nanosheets is indeed increased compared with that of Ni₂P. The results confirmed that the OER overpotentials and E_d energy levels are strongly correlated. Consequently, DFT simulations further indicated that slightly elevating the E_d energy levels balances the adsorption and desorption capacities of the oxygen-bearing intermediates (O*, OH*, and OOH*).

Based upon the preceding story, Co incorporation into the structure of layered VB₂ has remarkably influenced the OER performance compared to the parent counterpart. Still, based on similar works[155], the introduction of TM atoms into a host material can boost the catalytic competency to a certain extent (in the case of present work up to $x = 0.1$). The optimum value of E_d can be obtained in the case of V_{0.9}Co_{0.1}B₂, which leads to a superior OER performance compared to other samples. Further Co substitution may create undesired bonding of Co – Co rather than Co – B.

With the mentioned parameters in mind, an optimum amount of Co substitution ($x = 0.1$) in the framework of VB₂ has dramatically altered the electronic structure and drastically lowered the required overpotential to deliver a current density of 10 mA cm⁻², supported by EDS mapping (almost uniform distribution of Co all over the entire sample, see Figure B4). To examine the reaction kinetics of the fabricated electrocatalysts, the Tafel slopes were also calculated. Tafel slope and substitution concentration were in direct relation, meaning that higher Co contents exhibited higher Tafel slopes. For this, RuO₂ exhibited the smallest Tafel slope (61.1 mV dec⁻¹) relative to manufactured catalysts and V_{0.8}Co_{0.2}B₂ displayed the highest value (285.5 mv dec⁻¹) (refer to Figure 4.

6b). Based upon the observations from Figure 4. 6a and b, the $V_{0.9}Co_{0.1}B_2$ sample owns the highest performance towards OER.

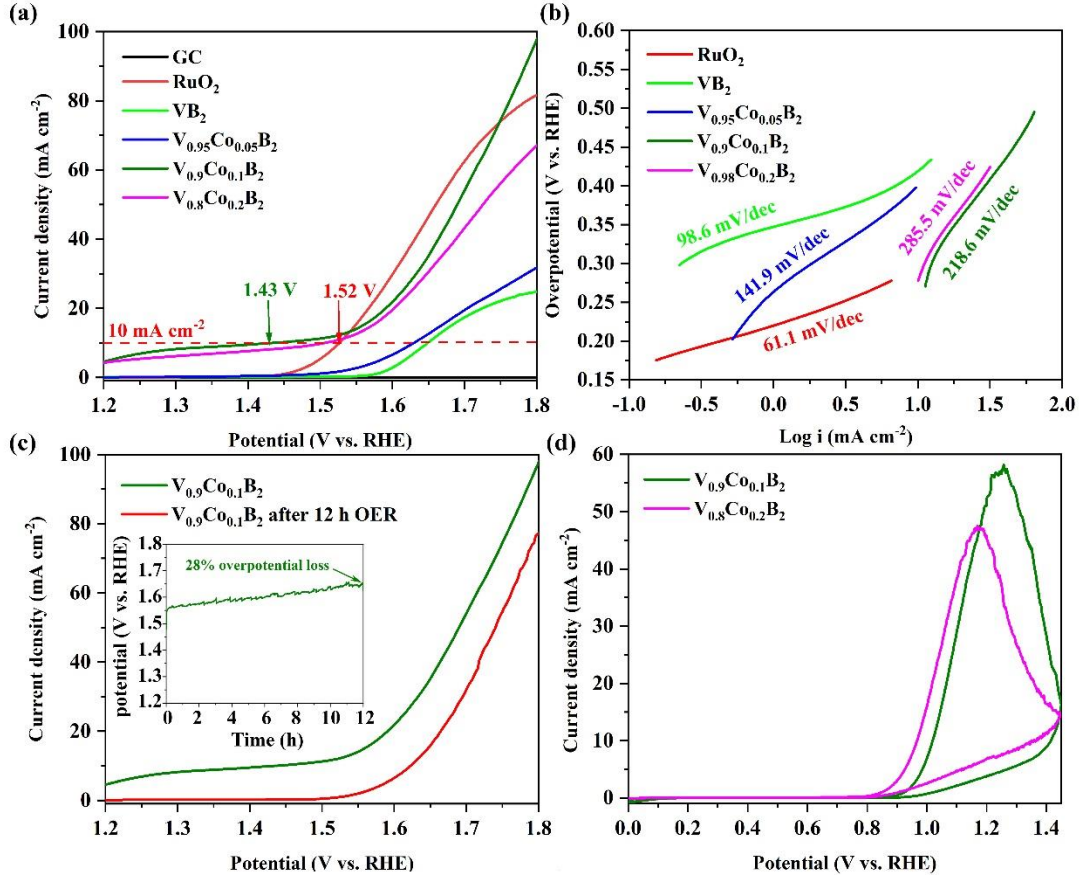


Figure 4. 6. Electrochemical studies of $V_{1-x}Co_xB_2$ ($x = 0, 0.05, 0.1$, and 0.2) at a scan rate of $5\ mV\ s^{-1}$ in $1\ M\ KOH$ a) Polarization curves, b) Tafel plots, c) OER for $V_{0.9}Co_{0.1}B_2$ before and after 12 h water oxidation operation, and d) CV experiments for $V_{0.9}Co_{0.1}B_2$ and $V_{0.8}Co_{0.2}B_2$.

The best-performing electrode was exposed to a current density of $10\ mA\ cm^{-2}$ under $1\ M\ KOH$ conditions, illustrating decent durability after 12 h (refer to Figure 4. 6c). The required potential to derive water oxidation was increased from 1.43 V (before long-run durability) to 1.63 V. To our surprise, the surface of constructed electrode did not go under obvious deterioration (SEM images from Figure B6). In order to explain the story behind the extraordinary performance of $V_{0.9}Co_{0.1}B_2$, we conducted CV experiments in the OER region ($0 - 1.45\ V$) at a rate of $5\ mV/s$. It is firmly validated by previous experimental and theoretical studies that a peak in the range of $1 - 1.3\ V$ vs. RHE is correlated to the following reversible redox processes $M(OH)_2 + OH^- \leftrightarrow MOOH + H_2O + e^-$ (M refers to divalent TM).[139, 156] Concerning current work, however, an irreversible peak was discerned around 1.3 V, verifying the formation of $V_{0.9}Co_{0.1}(OH)_2/V_{0.9}Co_{0.1}OOH$ and/or $Co(OH)_2/CoOOH$ layers, functioning as active water oxidation

sites on the surface (refer to Figure 4. 6d). A myriad number of reports claimed that Co oxy-hydroxide layer plays an active-site role on the surface of cobalt-boride catalysts.[92, 113, 145, 156-158] In other words, the presence of B—more electronegative relative to V and Co—induces reverse electron transfer to d -band of Co (or V), suppressing the formation of stable oxide phases and initiating the in-situ existence of oxy-hydroxides.[159] Nevertheless, a 0.2 V drop in overpotential after 12 h operation corroborates the partial degradation of oxy-hydroxy phases. It has also evinced that self-aggregation behavior is a principal culprit for the defective performance of sole 3d TMs, alloys, oxides, and hydroxides during long-run electrochemical processes.[160]

The electrochemical impedance spectroscopy (EIS) was performed to inspect the charge transfer resistance. The results of fitting data by ZView software are tabulated in Table 4. 1. In this table, Re, CPE, Rct, and W denote the resistance of the solution between the working and reference electrodes, interfacial capacitive component, Faraday resistance, and Warburg impedance, respectively. The recorded EIS curves unveiled two distinctive types of behaviors. Figure 4. 7a demonstrates the Nyquist plots with their representative equivalent circuits. Based upon the analysis of the charge transfer behavior of the investigated electrocatalysts, we can conclude that VB_2 and $\text{V}_{0.95}\text{Co}_{0.05}\text{B}_2$ follow the equivalent circuit (i), pointing out that diffusion is the controlling step on the surface. In sharp contrast, $\text{V}_{0.9}\text{Co}_{0.1}\text{B}_2$ and $\text{V}_{0.8}\text{Co}_{0.2}\text{B}_2$ catalysts conform to the equivalent circuit (ii), suggesting a capacitive manner.

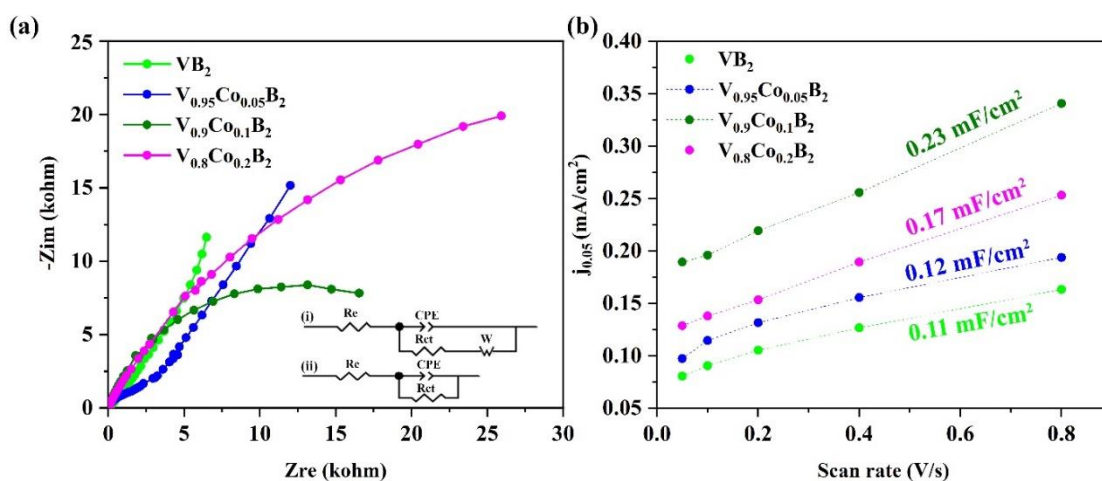


Figure 4. 7. a) EIS plots and b) Capacitive currents from CV measurements plotted as a function of scan rate.

In this context, the results summarized in Table 4. 1 and shown in Figure 4. 7a are in good agreement with other electrochemical measurements. As shown in Figure 4. 7a, the

Nyquist plot of $V_{0.9}Co_{0.1}B_2$ displays the smallest semicircle diameter, manifesting the lowest total resistance because of its high capacitance (about $10^{-4} \text{ mFsp}^{-1}$). It must be noted that the larger capacitance of $V_{0.9}Co_{0.1}B_2$ can partially be attributed to the larger specific surface area (Figure 4. 7b). For this, capacitive current at 0.05 V (vs RHE) against the scan rate was plotted, and corresponding C_{dl} values were estimated through the linear fitting of the plots (refer to supporting information, Figure B7). Following trend can be drawn into attention VB_2 (0.11 mF cm^{-2}) < $V_{0.95}Co_{0.05}B_2$ (0.12 mF cm^{-2}) < $V_{0.8}Co_{0.2}B_2$ (0.17 mF cm^{-2}) < $V_{0.9}Co_{0.1}B_2$ (0.23 mF cm^{-2}) which is in line with above-written OER results.

Pristine VB_2 in spite of owing smaller particle size compared to other samples (refer to Figure 4. 2 and Figure 4. 3), suffers from an insignificant electrochemically active surface area (ECSA) which means particle size and ECSA are not necessarily in direct relation. That is to say, besides average particle size, other factors such as the nature of the alloying component of particles also play a role. It was stated that catalysts—Pt/C and PtM/C catalysts[161]—are either materials with metallic nanoparticles or those whose metallic surfaces are covered by oxide/hydroxide compounds. For the latter group, the metallic surfaces could be partially insulated with oxides. When looking at the VB_2 and $V_{1-x}Co_xB_2$, based on the XPS results (Table B2), the substitution of V with Co mitigated the oxygen amount on the particle surface. Investigated VB_2 has higher portion of oxygen (53.06 %) compared to the $V_{1-x}Co_xB_2$ powders (35.62, 33.33 and 32.21 % for $x = 0.05$, 0.1, and 0.2 respectively), therefore it is more likely to undergo insulation with oxide/hydroxide compounds. The phenomenon adversely affects the ECSA parameter in parent VB_2 . On the contrary, Co-incorporated samples are less likely to experience insulation and thereby benefit from higher ECSA. In addition to this, a uniform nanoparticle spatial distribution and the degree of their agglomeration could depend on their composition.[161, 162] For the $V_{1-x}Co_xB_2$ powders, the powder morphology with an irregular shape not only can suppress the agglomeration of powder on the electrode surface but also increase the electrode surface area.

Table 4. 1. Calculated values of the equivalent circuit elements for the samples.

Sample	Re (Ω)	CPE-T (mFsp^{-1})	CPE-P	Rct (Ω)	W-R (Ω)
VB ₂	13.84	3.1×10^{-5}	0.8	3446	17000
V _{0.95} Co _{0.05} B ₂	13.28	1.1×10^{-5}	0.94	2317	9230
V _{0.9} Co _{0.1} B ₂	15.72	9.4×10^{-5}	0.78	18000	-
V _{0.8} Co _{0.2} B ₂	12.63	3.4×10^{-5}	0.74	48000	-

4.4. Investigation of OER Catalytic Mechanism

To gain insight into the mechanism of OER, the FE of OER concerning the V_{0.9}Co_{0.1}B₂ was developed by RRDE, in which the generated oxygen at the disk electrode was moved from the disk electrode (target catalyst on GC electrode) to the Pt ring electrode where it was reduced. The applied potential (0.2 V vs. RHE) to the ring electrode was adequately negative to reduce the generated oxygen immediately, and the currents were recorded (ring and disk current) in terms of the potential of the disk electrode. The disk electrode was maintained at a constant potential within the region of 1.45 – 1.6 V (vs. RHE) with an interval of 0.05 V (vs. RHE) for sequential periods of 60 s each, while rotating at 1600 rpm under an N₂ gas blanket. To estimate the FE, the following equation was employed:

$$\text{FE} = \frac{2i_r}{i_d N} \quad (3)$$

where i_r and i_d represent the respective measured ring and disk currents—N was defined in the experimental section. Figure 4. 8a and b feature the plots of the disk and ring currents along with calculated efficiency values of the V_{0.9}Co_{0.1}B₂ through OER under 1.0 M KOH as a function of the applied disk potential, respectively. From Figure 4. 8b, the OER initiates at a very low potential of 1.45 V (vs. RHE), yielding ~ 44 % FE. With increasing the applied disk potential to 1.50 V (vs. RHE), FE reached ~ 80 %, suggesting that the OER is dominant in disk current rather than side reactions (e.g., further oxidation of the catalyst). With the disk voltage increased to 1.55 V (vs. RHE), efficiency also increased to a maximum value of ~ 97 %, signifying an enhancement in the dominant content of oxygen generation. Consequently, based on the FE examinations in N₂-saturated 1.0 M KOH, a potential window of 1.50 – 1.55 V (vs. RHE) is preferable for

the evolution of oxygen on the $V_{0.9}Co_{0.1}B_2$ catalyst. Eventually, raising the potential to 1.60 V (vs. RHE) caused a meaningful drop from $\sim 97\%$ to $\sim 80\%$ in FE value. The primary reason behind this deficiency is likely the large number of undissolved oxygen bubbles generated at the relatively high applied disk potential which might not be collected efficiently by the Pt ring electrode.

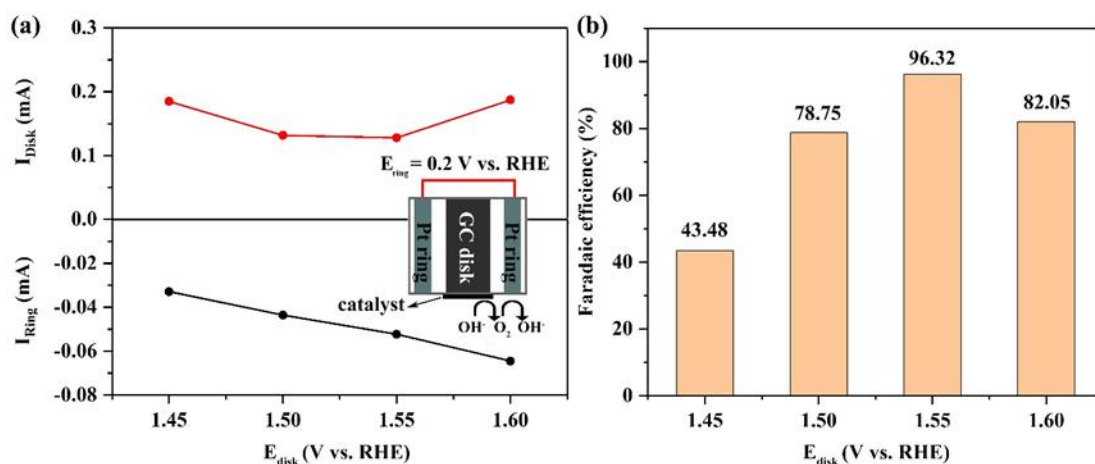


Figure 4. 8. Faradaic efficiency of the catalyst in 1 M KOH at 1600 rpm under N_2 saturation, a) The disk and ring currents of RRDE plotted as a function of the applied disk potential, and b) The calculated Faradaic efficiency.

4.5.CONCLUSIONS

In brief, the Co-substituted VB_2 with the formal composition of $V_{1-x}Co_xB_2$ ($x = 0, 0.05, 0.1$, and 0.2) were developed via a straightforward and scalable carbothermal reduction technique. Amongst obtained electrocatalysts, $V_{0.9}Co_{0.1}B_2$ exhibited superior OER activity to RuO_2 , demanding only 200 mV to reach the current density of 10 mA cm^{-2} . The primary reason behind this outstanding performance is the drastic transformation of morphology of virgin VB_2 following Co substitution, which resulted in more catalytically active sites, confirmed by electrochemical surface area analysis. In addition, benefiting from low charge transfer resistance, the optimal substitution of Co into the structure of layered VB_2 , efficient charge transfer between V, Co, and B, along with the in-situ formation of $V_{0.9}Co_{0.1}(OH)_2$ / $V_{0.9}Co_{0.1}OOH$ and/or $Co(OH)_2/CoOOH$ layers on the surface, $V_{0.9}Co_{0.1}B_2$ realized the supreme electrocatalytic water oxidation under alkaline medium. Furthermore, the best-performing catalyst illustrated satisfactory long-run stability under OER operation in 1.0 M KOH solution. The obtained results which are far better than most documented metal boride-derived catalysts may create a new and cost-effective path for the practical realization of OER electrocatalysts.

CHAPTER 5

DESIGNING IN-SITU GROWN TERNARY OXIDE / 2D Ni-BDC MOF NANOCOMPOSITES ON NICKEL FOAM AS EFFICIENT ELECTROCATALYSTS FOR ELECTROCHEMICAL WATER SPLITTING



The majority of this chapter has been published in *ACS Materials Au*, 2022, 3(2), 143-163. The original manuscript has been rearranged to conform to the format requirements of the dissertation.

5.1. Introduction

Despite the numerous advantages of 3d TM-derivative materials, their performance under strong basic/acidic conditions and high current densities is limited [19] and thus not practical for real applications. To overcome this impediment, the construction of a composite with other materials such as metal-organic frameworks (MOFs) with inherent mechanical stability could be a promising solution.[63-65] MOFs, a newly emerged family of crystalline coordination polymers composed of metal ions (e.g. Fe, Co, Ni, Cu) attached to organic ligands with tunable chemical composition, high electrochemical surface area, hollow structures, and controllable morphology,[14, 19] have gained fame for a variety of applications such as electrocatalytic water splitting,[66-68] gas storage,[69, 70] chemical sensing,[71, 72] supercapacitors,[73, 74] and metal-air batteries.[75-77] Regarding catalysis, the unstable coordinated solvent molecules in the MOF structure can easily detach in the course of the reaction and form coordinatively unsaturated metal centers (CUMCs).[78] Depending on coordinated metal components, the CUMCs may function as typical Lewis acid centers to demonstrate versatile catalytic activities. Yet, the poor electrical conductivities of MOFs (about 10^{-10} S m⁻¹)[79, 80] hamper their implementation in practice as efficient electrocatalysts for the OER and HER.[81-83]

To address the above-stated issue one approach is to load electrocatalytic MOFs on conductive substrates such as NF. The 3D open porous framework of NF with a large specific surface area and zigzag channels can further strengthen the electron and mass transport of in-situ grown MOFs on the NF backbone.[3] In fact, self-supported MOF electrocatalysts induce superior electrochemical performances compared to the powder-based systems with the binders such as Nafion,[14, 84, 85] which can be attributed to the synergistic effect between MOF-based composites and conductive host.[86] Additionally, the idea of binder-free hydrothermal synthesis of both ternary mixed TMOs and MOFs using NF as a substrate is interesting in that NF can function as a current collector for direct growth. Moreover, this strategy can minimize binder costs, reduce preparation time, boost ion transport, and strengthen the contact between electrocapacitive material and substrate. Furthermore, the 3D-order hierarchical nanostructure of MOF/ternary mixed TMOs induces remarkable structural stability and improves electron/ion mobility that are advantageous to obtain superior electrochemical features.[163] Not to mention that, so far, binary oxides of Ni-Co have been extensively

studied for the electrolysis of water. It should be noted that the addition of a third component (oxides of Fe, Cu, and Zn) could in principle demonstrate higher electrochemical performance owing largely to the enriched oxidation states and synergistic effects of the multi-metal components in the electrodes.[164]

In addition to the above-mentioned factors, the synergistic effect between host-guest type composite is another effective parameter to promote the performance of multicomponent composites in oxide electrocatalysts due to their inherently low electrical conductivities.[165] The strong adhesion of nanocomposite materials (guest) on a porous substrate like NF (host) can enlarge the electroactive surface area and boost the electron transfer within the structure. Keeping these in mind, we herein focus on the architecture of an entirely novel nanocomposite based on Ni-Co-M oxide ($M = \text{Fe, Cu, Zn}$)/Ni-BDC MOF@NF (see Figure C1 as an instance) for highly efficient OER, HER, and overall water splitting. For the construction of the electrocatalysts, a simple two-step hydrothermal method was adopted. With this design, multiple synergistic effects between NF substrate, ternary Ni-Co-M oxide nanocomposite, and Ni-BDC MOF [$\text{Ni}_3(\text{OH})_2(\text{tp})_2(\text{H}_2\text{O})_4$] ($\text{tp} = \text{C}_8\text{H}_4\text{O}_4^{2-}$)[166, 167] could be presumed. From the electrochemical experiments under an alkaline medium, Ni-Co-Fe oxide/Ni-BDC@NF generated a current density of 10 mA cm^{-2} at an ultra-low overpotential (η) of 120 mV toward OER, Ni-Co-Zn oxide/Ni-BDC@NF afforded the 10 mA cm^{-2} at a small overpotential of 170 mV toward HER, and finally, once these two best OER and HER catalysts were combined to drive overall water splitting, the couple demanded only a cell voltage of 1.58 V to deliver 10 mA cm^{-2} .

5.2.EXPERIMENTAL SECTION

5.2.1. Catalyst Fabrication

5.2.1.1.Materials

1,4-benzenedicarboxylic acid (terephthalic acid/1,4-BDC, Sigma Aldrich, 98%), N,N-dimethylformamide (DMF, Sigma Aldrich), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma Aldrich, 99.999% trace metals basis), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma Aldrich, 99.999% trace metals basis), iron nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Sigma Aldrich, $\geq 99.95\%$ trace metals basis), zinc hydroxide nitrate ($\text{Zn}(\text{OH})(\text{NO}_3) \cdot \text{H}_2\text{O}$), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma Aldrich, 98%), copper nitrate hexahydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, Sigma Aldrich, 99.999% trace metals

basis), and urea ($\text{CH}_4\text{N}_2\text{O}$, Sigma Aldrich, $\geq 98\%$) were utilized without any prior treatment.

5.2.1.2. Synthesis of Ni-BDC@NF

The commercial NF with a size of $2\text{ cm} \times 3\text{ cm}$ was ultrasonically treated with 2.0 M HCl solution, acetone, deionized (DI) water, and ethanol each for 10 min to get rid of impurities such as oxide on the NF surface, and dried in the open air. To grow Ni-BDC on NF, two solutions were simultaneously prepared by dissolving 5 mmol of 1,4-BDC in 15 mL of DMF (solution 1) and 5 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 15 mL of DI water (solution 2) under vigorous stirring for 30 min. Thereafter, solution 1 was mixed with solution 2 and they were stirred for another 30 min. The homogeneous resulting solution was then ultrasonicated for 60 min and transferred to a 50 mL Teflon-lined stainless-steel autoclave containing a pretreated piece of NF. The sealed batch was kept at $180\text{ }^\circ\text{C}$ for 24 h and cooled down naturally to room temperature. The obtained product was washed thoroughly with DMF, DI water, and ethanol and vacuum dried overnight at $70\text{ }^\circ\text{C}$.

5.2.1.3. Synthesis of Ni-Co-M Oxide ($M = \text{Fe}, \text{Cu}, \text{Zn}$)@NF

For the growth of Ni-Co-M oxide ($M = \text{Fe}, \text{Cu}, \text{Zn}$) on NF, a simple one-step hydrothermal procedure was adopted. For this, a specified amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol), metal nitrate hydrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1 mmol) or $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (1 mmol) or $\text{Zn}(\text{OH})(\text{NO}_3) \cdot \text{H}_2\text{O}$ (1 mmol)], and $\text{CH}_4\text{N}_2\text{O}$ (8 mmol) were added to a 100 mL beaker containing 40 mL DI water and stirred for 2 h to receive precursor solution. The solution was then transferred to a 50 mL Teflon-lined hydrothermal autoclave in which a piece of NF was placed. The autoclave system was sealed and maintained at $180\text{ }^\circ\text{C}$ for 10 h and quenched naturally to room temperature. The resultant sample was rinsed several times with DI water and ethanol and was dried overnight in a vacuum oven at $60\text{ }^\circ\text{C}$. The mass-loading of Ni-Co-M oxide@NF was $< 5\text{ mg cm}^{-2}$. At this point for convenience, the labeling of the nanocomposites is regarded as NCF, NCC, and NCZ for respective nanocomposites of Ni-Co-Fe oxide, Ni-Co-Cu oxide, and Ni-Co-Zn oxide. It is worth noting that we prepared another sample as NCZ' with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as zinc source through the above-written procedure and performed the electrochemical measurements. Due to the poor electrocatalytic activity of NCZ', we did not conduct further experiments.

5.2.1.4. Synthesis of Ni-Co-M (M = Fe, Cu, Zn) Oxide/Ni-BDC@NF Nanocomposites

For the fabrication of Ni-Co-M oxide/Ni-BDC on NF, the same procedure as for the growth of Ni-BDC@NF was followed. Once the stirring of solution 1 + solution 2 was completed, a certain amount of already prepared powder of Ni-Co-M (15 wt. %) was added to the solution mixture and stirred for 60 min. The solution was further mixed by ultrasonic vibrations for another 60 min. The precursor solution was transferred to a 50 mL Teflon-lined autoclave reactor and heated at 180 °C for 24 h. Following the completion of the reaction, the treatment of the produced materials was identical to that of Ni-BDC@NF. The mass-loading of Ni-Co-M oxide/Ni-BDC@NF was about 10 mg cm⁻². To preclude redundancy, from this point, the following labeling is considered; NCF/Ni-BDC@NF, NCC/Ni-BDC@NF, and NCZ/Ni-BDC@NF for respective nanocomposites of Ni-Co-Fe oxide/Ni-BDC@NF, Ni-Co-Cu oxide/Ni-BDC@NF, and Ni-Co-Zn oxide/Ni-BDC@NF.

Figure C1 schematically presents the coupling process of Ni(OH)₂ as one of the dominant phases in NCF with Ni-BDC ligand. As the DMF solvent is slightly acidic, Ni(OH)₂ partially loses its hydroxyl groups under sonication, resulting in Ni^{δ+} and OH^{δ-}. Then OH^{δ-} attracts the protons (H⁺) of the BDC ligand to release the H₂O molecule. Next, deprotonated BDC ligands can react with unsaturated Ni^{δ+} to form Ni(OH)₂/Ni-BDC. Similar interactions can take place for other phases to create heterostructures between Ni-BDC and ternary mixed oxides.

5.2.1.5. Preparation of the RuO₂@NF and Pt/C@NF Electrocatalysts

Commercial RuO₂ (5 mg) was dispersed in a 1000 μL solution of ethanol and DI water (700:300) and sonicated for 30 min followed by the addition of 20 μL Nafion solution with another 30 min sonication to achieve a homogenous ink. Similarly, 20% Pt/C (5 mg) was sonicated for 30 min in a 1000 μL solution of ethanol and DI water (600:400) and 20 μL Nafion solution was added to the solution with 30 min further sonication. The prepared ink was dipped on a piece of NF to receive a mass-loading of about ~5 mg cm⁻².

5.2.2. Catalyst Characterization

The crystalline planes of the resultant powders were identified by a Rigaku Mini Flex 600 X-ray diffractometer, Cu Kα radiation (λ = 1.5418 Å). XRD patterns were recorded in the 2θ range of 5–70° at a scanning rate of 5° min⁻¹. The morphology of the catalysts

grown on the NF was characterized by an FESEM;Zeiss Ultra Plus) connected to a Bruker Xflash 5010 (123 eV spectral resolution) EDS detector. The quantitative concentrations of transition metals within the structure of ternary mixed oxides were characterized by BRUKER TIGER S8 wavelength dispersive X-ray fluorescence spectrometer. The microstructure of the samples scraped off the NF was in addition examined by transmission electron microscopy (TEM;Thermo Scientific Talos F200S 200 kV TEM). The SAED image was obtained via a Thermo Scientific Talos F200S 200 kV TEM instrument. Besides, the lattice fringes of the revealed nanoparticles were specified by the high resolution-transmission electron microscopy (HR-TEM) photographs taken by the same apparatus. In addition, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and the associated EDS elemental mappings were conducted on a Hitachi HT7800 (TEM) with EXALENS (120 kV) working at HR mode. To determine the thickness of a single nanosheet, AFM was carried out using Bruker Dimension Icon AFM. The surface compositions of the powdered samples were analyzed on a Thermo Scientific K-Alpha. XPS with an Al K α monochromator source (1486.6 eV). The deconvolution of the XPS spectra was carried out through Avantage 5.9 software and all spectra were corrected according to the binding energy (BE) of C 1s = 284.5 eV. To distinguish the functional groups, a JASCO 6800 FTIR full vacuum & FTIR microscope apparatus was employed and the spectra were recorded in the wavenumber region of 4000 to 400 cm⁻¹. To determine the BET specific surface area of the powder products through N₂ adsorption-desorption isotherms, a Micromeritics ASAP 2010 instrument was exploited. Finally, ICP-MS Agilent 7700x was conducted to study the trace amount of dissolved TMs in an alkaline solution for post-stability tests.

5.2.3. *Electrochemical Characterization*

The electrochemical studies were performed on an an AutoLab Potentiostat Galvanostat (PGSTAT302N, made in the Netherlands) in a typical three-electrode system using catalysts grown on NF (0.5 cm × 1 cm) as working electrodes, Pt spring as the counter electrode, and RHE; HydroFlex as the reference electrode in alkaline conditions (1.0 M KOH). The LSV curves were recorded at a scan rate of 5 mV s⁻¹ to evaluate the electrocatalytic performance. The OER overpotentials (η) at a fixed current density (j) were calculated based on $\eta_{\text{OER}} = E_{\text{RHE}} - 1.23 \text{ V}$, within the OER potential window (1.2 to 1.8 V) and the HER overpotentials were demonstrated according to $\eta_{\text{HER}} = E_{\text{RHE}}$, in the

HER potential region (0 to -1 V). The Tafel slopes were achieved by replotting the LSV curves, η as a function of $\log(j)$ via the Tafel equation ($\eta = a + b \log j$, where b is the Tafel slope.)[7]

The OER and HER longevity experiments were carried out via chronopotentiometry at a fixed j of 10, 20, and 50 mA cm⁻². EIS was recorded at the potential of 0 V with a sinusoidal amplitude of 10 mV at a frequency ranging from 100 kHz to 0.1 Hz. The ECSA was acquired through the C_{dl} with respect to the CV measured at various scan rates of 80, 100, 120, 140, 160, 180, and 200 mV s⁻¹ across the potential window from 0.7 to 0.8 V vs RHE. All the electrochemical data were presented without iR correction. Finally, gas products (H₂/O₂) for the full-cell water electrolysis were detected and quantified using a gas chromatograph (7820A, GC-System, Agilent) equipped with a thermal conductivity detector (TCD).

5.3.RESULTS AND DISCUSSION

5.3.1. Chemical Studies

The synthetic procedures to produce ternary oxides and nanocomposites are thoroughly described in the experimental section. The schematic image (Figure 5. 1a) manifests the two-step hydrothermal process to directly grow the nanocomposites of NCM/Ni-BDC@NF (N=Ni, C=Co, M: F=Fe, C=Cu, and Z=Zn, BDC: benzene dicarboxylic acid, NF: Nickel foam). The colorful growth of bare Ni-BDC, ternary oxide NCM, and NCM/Ni-BDC nanocomposite on NF indicates the successful coverage of all investigated materials on the substrate (Figure 5. 1b). SEM was employed to better understand the morphology of materials grown on NF. From the high-magnification photograph in Figure 5. 1c the heavily stacked lamellar sheets of Ni-BDC can be visualized which is in line with previous reports.[15, 168] The inset image shows the coverage of Ni-BDC on the 3D macroscopic porous backbone of NF substrate, the pore width of which can reach several hundreds of micrometers.

Figure 5. 1d-f depicts the microstructure of NCM@NF. For these materials, urea is a crucial ingredient in a typical hydrothermal recipe. Following the mixing of the starting materials and once the metal ions including Ni²⁺, Co²⁺, and Mⁿ⁺ (Mⁿ⁺ = Fe³⁺, Cu²⁺, Zn²⁺) absorb on the NF surface, urea slowly decomposes into hydroxyl and carbonate anions to adjust pH. In this sense, metal ions are involved in the reaction with anions and produce the Ni-Co-M precursor. With the reaction going forward, the concentration of anions

declines in the reaction which brings about an array of nanowire morphology for Ni-Co-Fe[169] and urchin-like morphology for Ni-Co-Cu and Ni-Co-Zn[170, 171] which can be seen respectively in Figure 5. 1d-f. The diameter of the nanowires was estimated to be 20–60 nm, while the diameter of nanoneedles was in the range of 40–90 nm. In addition, the inset images reveal the full coverage of the NF skeleton with a uniform thin layer of ternary oxide. From the low-magnified micrographs (inset of Figure 5. 1d-f and Figure C2) the NF-templated 3D nanostructure of metal oxides can furnish a 3D interconnected pathway for the facilitated mass and electron transfer during faradaic redox reactions.[172] It must be noted that previous studies calcined the materials on NF, nonetheless, in this work, except for Ni-Co-Zn oxide@NF (NCZ), we avoided the calcination step for the sake of electrochemical examinations.

The topographies of NCM/Ni-BDC@NF are portrayed in Figure 5. 1g-i. It is evident that the closely packed lamellar morphology is maintained after the addition of ternary oxide into the 3D structure of Ni-BDC. A comparison of inset images of Ni-BDC@NF and NCM@NF with NCM/Ni-BDC@NF suggests that the coverage of NCM/Ni-BDC nanocomposites on NF is relatively thicker. Besides, microstructural imaging in Figure C2 represents the growth of ternary metal oxides on the NF backbone at lower magnification, featuring a better view of the metal oxides' coverage of NF. Likewise, Figure C3 portrays a top-view SEM image of blank Ni-BDC and its nanocomposites, revealing the dense deposition of layers on NF substrate with poor porosity. What is more, the EDS elemental mappings were performed on a large portion of materials on the NF substrate to show the distribution of all elements throughout the entire substrate (see Figures C4 and C5). Eventually, the X-ray fluorescence spectrometry (XRF) quantified the concentrations of transition metals within the structure of NCM and the results were tabulated in Table C1. The presence of excess Ni compared to other elements is not surprising, demonstrating the Ni extraction from NF under heat and pressure during the hydrothermal procedure.

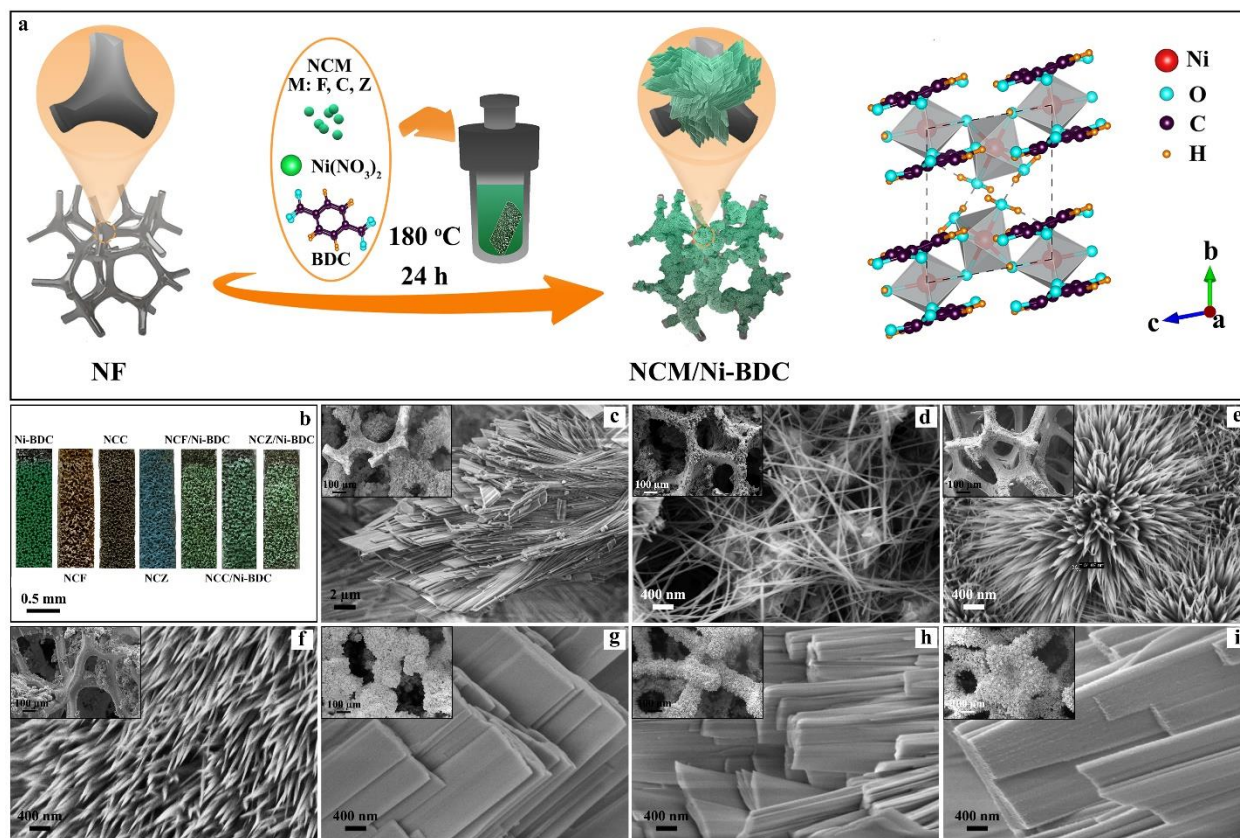


Figure 5. 1. a) Schematic illustration of nanocomposite catalyst fabrication, NCM/Ni-BDC @NF (N=Ni, C=Co, M: F=Fe, C=Cu, and Z=Zn, BDC: benzene dicarboxylic acid, NF: Nickel foam), b) Digital photographs of various in-situ grown catalysts on NF with distinctive colors, c, d, e, f, g, h and i) SEM images of Ni-BDC, NCF, NCC, NCZ, NCF/Ni-BDC, NCC/Ni-BDC, and NCZ/Ni-BDC respectively, (inset: low magnification images show the growth of catalyst on NF skeleton)

Figure 5. 1a illustrates the crystal structure of Ni-BDC along the a-axis, residing in the triclinic system (space group $P-1$).^[173] The material demonstrates a layered arrangement perpendicular to the b-axis and parallel to the ac plane. Each layer consists of 1D corner sharing Ni(II)O₆ octahedra chains elongated along the c-axis and joined to one another through bridging bidentate tp = C₈H₄O₄²⁻ anions along the a-axis. Layers are connected by hydrogen bonds between Ni-coordinated water molecules with which the integrity of the structure is sustained. In this structure, the most intense plane (100) provides the most exposed structure for the electron transfer and diffusion of electrolyte solution. The 1D Ni(II)O₆ octahedra chains along the c-axis create a conductive route for electrons, and at the same time the layers parallel to the ac plane—with interspaces between each layer—facilitate the storage and diffusion of electrolyte solution. Such a layered and sophisticated structure can be beneficial for electrochemical applications.^[166]

XRD is an excellent tool to examine the chemical composition and crystallographic structure of as-obtained materials. The XRD patterns of ternary oxide NCM—scratched off from NF—can be visualized in Figure C6. As demonstrated in this figure, the XRD peaks of NCF can be constructed from Fe_2O_3 (Card No.: 72-0469) (at 2-theta of 23.03, 32.86, and 54.08° corresponding to (012), (104), and (116)), spinel ferrite, Fe_3O_4 (Card No.: 74-0748) (at 2-theta of 30.33, 35.64, 57.34, and 62.89° relating to (220), (311), (511), and (440)), $\text{Co}_2(\text{OH})_2\text{CO}_3$ (at 2-theta of 14.60, 17.44, 24.12, 27.68, 34.65, 32.80, 36.56, 39.65, 42.06, 43.41, 48.96, 51.86, 59.74, and 61.04° pertaining to (020), (120), (220), (001), (121), (-211), (330), (221), (250), (-241), (260), (401), (-212), and (370), refer to [174]), and $\text{Ni}(\text{OH})_2$ (Card No.: 38-0715) (at 2-theta of 11.34, 23.03, 38.78, and 46.03° indexing to (003), (006), (015), and (018)) phases. In the case of NCC, the possible phases in the sample were identified to be CuO (Card No.: 73-6023) (at 2-theta of 35.43, 38.60, and 49.39° assigning to (-111), (111), and (-202)), $\text{Cu}(\text{OH})_2$ (Card No.: 72-0140) (at 2-theta of 33.86, 39.71, 53.90, 56.17, and 62.60° belonging to (002), (130), (132), (151), and (200)), and $\text{Cu}_2(\text{OH})_2\text{CO}_3$ (Card No.: 72-0075) (at 2-theta of 14.65, 17.46, 24.11, 28.02, 29.65, 30.70, 36.56, 42.14, 44.98, 47.42, 50.93, and 59.92° appertaining to (020), (120), (220), (011), (310), (-201), (330), (250), (-411), (-151), (520), and (-361)). It is important to mention that $\text{Co}_2(\text{OH})_2\text{CO}_3$ and $\text{Cu}_2(\text{OH})_2\text{CO}_3$ are isostructural and both may contain some Cu or Co species in their structures which cannot be easily distinguished by the XRD patterns. Interestingly, $\text{Co}_2/\text{Cu}_2(\text{OH})_2\text{CO}_3$ has a typical nanowire-like structure, and according to several reports, this structure encompasses a large number of active sites for an electrocatalytic reaction.[175-177] Regarding the NCZ, the reflections were found to be consisting of spinel-type ZnCo_2O_4 (Card No.: 73-1702) (at 2-theta of 36.40, 44.50, and 59.74° correlating with (331), (400), and (511)), NiOOH (Card No.: 9012319) (at 2-theta of 12.95 and 24.98° connecting with (111) and (222)), and CoCO_3 (Card No.: 78-0209) (at 2-theta of 33.28, 38.62, 42.84, 46.77, 53.76, and 62.16° corresponding to (104), (110), (113), (202), (116), and (122)). Finally, it is of high significance to note that we also detected metallic Zn via XRD at 2-theta angles of around 36.32, 39.15, and 43.25°.

It is not surprising to receive multiple oxides and hydroxides prior to calcination. Besides, there might be a very minor peak shift in the peak positions of ternary mixed oxides which can be attributed to partial substitution of the elements in their structures. As mentioned above, calcination removes nearly all $-\text{OH}^-$ and $-\text{CO}_3^{2-}$ species, conducting the formation of ternary oxide which in terms of crystal structure resembles that of cubic Co_3O_4 .^[169-171, 178] For this, we likewise examined the XRD pattern of a representative

sample after calcination at 350 °C for 5 h. The XRD pattern of this sample is identical to the reported Co_3O_4 phase (see Figure C7a). However, as mentioned earlier, the materials' preparation in this work does not include the calcination step.

In addition, the XRD patterns of pure Ni-BDC and NCM/Ni-BDC nanocomposites displayed all Bragg reflections related to Ni-BDC, validated by earlier reports (see Figure 5. 2a).[15, 166, 168] The coupling of NCM with Ni-BDC resulted in a slight shift in peak positions that we can observe in Figure 5. 2b. The interaction mechanism of MOF ligand and $\text{Ni}(\text{OH})_2$ was discussed by Zhu et al.[179] which can be generalized for other phases (refer to Experimental Section). Interestingly the (010) for NCF/Ni-BDC shifted to higher 2-theta angles, while for NCC/Ni-BDC and NCZ/Ni-BDC shifted to lower 2-theta angles. This might be explained by the comparison of ionic radii of host metal atoms. Ni^{2+} (69 pm), with heteroatoms, Co^{2+} (74.5 pm), Fe^{3+} (64.5 pm), Cu^{2+} (73 pm), and Zn^{2+} (74 pm). It can be presumed that partial substitution of Ni^{2+} by Fe^{3+} with smaller atomic radius and Ni^{2+} by $\text{Cu}^{2+}/\text{Zn}^{2+}$ with larger atomic radii in the structure of their relevant nanocomposites have induced the modification on the lattice constants of Ni-BDC (host) according to the Bragg's law.[180] In the meantime, the XRD patterns of NCZ' and its corresponding nanocomposite, NCZ'/Ni-BDC, can be seen in Figure C7b.

The surface chemical composition and electronic structure of Ni-BDC and Ni-BDC-derived nanocomposites were determined through XPS. The survey spectra verified the appearance of constituent elements in each sample which is to a great extent consistent with EDS analysis. For blank Ni-BDC (Figure C8), the high-resolution XPS spectrum of C 1s was deconvoluted into three peaks located at binding energies (BEs) of 284.5, 285, and 288.2 eV which can respectively be indexed to $\text{C}=\text{C}$ (sp^2), $\text{C}-\text{C}$ (sp^3), and carboxylate carbon ($\text{O}=\text{C}-\text{OH}$) bonds, signifying the presence of terephthalic acid.[181-184] The core-level Ni 2p XPS spectrum can be divided into two doublet components, Ni $2\text{p}_{3/2}$ and Ni $2\text{p}_{1/2}$ each containing a shake-up satellite peak. For this, two peaks at 855.6 and 872.9 eV are related to Ni^{2+} and the other pair at 856.6 and 874.9 eV are correlated to Ni^{3+} .[15]

According to the literature, Ni^{2+} can be originated from $\text{Ni}(\text{OH})_2$ [168] while Ni^{3+} can be stemmed from the octahedral coordination of Ni atoms with terephthalates in the Ni-BDC 3D structure.[185] The satellite peaks emerged at 861.7 and 879.5 eV,[186, 187] manifesting the existence of nickel-oxygen species.[188] To explore the presence of surface oxygen content in pure Ni-BDC, the O 1s spectrum was analyzed. The appearance of three peaks at BEs of 531.2, 532.2, and 533.08 eV were respective signals of Ni-O, O-C=O, and absorbed water species (refer to Figure C8).[189] Concerning NCF/Ni-

BDC, first we consider NCF in which Ni 2p, Co 2p, and Fe 2p spectra have been separated into two doublet peaks, one at lower BE ($2p_{3/2}$) and the other at higher BE ($2p_{1/2}$) (see Figure 5. 2c). The spin-orbit splitting values of Ni 2p (Δ_{Ni}), Co 2p (Δ_{Co}), and Fe 2p (Δ_{Fe}) were roughly 17, 15, and 13 eV, confirming the coexistence of both oxidation states of $2+$ and $3+$.^[10, 190, 191] Comparison of NCF/Ni-BDC (Figure 5. 2d) with NCF reveals that the Ni 2p, Co 2p, and Fe 2p peaks in NCF/Ni-BDC shifted to higher BEs, demonstrating the lower electron density of Ni, Co, and Fe atoms in NCF/Ni-BDC and thereby stronger electronic interactions between NCF and Ni-BDC. For the O 1s in NCF, three peaks centered at 529.4, 531.08, and 531.9 eV correspond to M–O bonds,^[170, 178] defective sites with low oxygen coordination (oxygen deficiency),^[16, 192] and absorbed water molecules,^[183] separately (see Figure C9a). Further, the analyzed XPS survey, C 1s, and O 1s spectra for NCF/Ni-BDC are portrayed in Figure C9b.

To fit the suitable bonds to the appeared spectra of NCZ/Ni-BDC, initially, the peak fitting of NCZ is discussed. For this, Figure 5. 2e shows Ni 2p and Co 2p spectra are marked with two oxidation states of $2+$ and $3+$. However, for the core-level Zn 2p XPS spectrum, we observed four peaks: lower BEs (1022.08 and 1023.9 eV) and higher BEs (1045 and 1046.9 eV) with Δ_{Zn} of approximately 23 eV pertaining to metallic Zn (Zn^0) and Zn^{2+} .^[193] From this, we can infer the presence of Zn^{2+} in $ZnCo_2O_4$ which was also verified by the XRD. After coupling NCZ with Ni-BDC, nearly all XPS spectra for the obtained nanocomposite shifted to lower BEs compared to those of NCZ (about 1 eV), reflecting lower oxidation states of Ni, Co, and Zn atoms in NCZ/Ni-BDC (Figure 5. 2f). This finding means that Ni, Co, and Zn possess higher electron densities in NCZ/Ni-BDC as opposed to NCZ. The XPS survey, C 1s, and O 1s of the above-discussed ternary oxide and corresponding nanocomposite were deconvoluted and visualized in Figures C9c and C9d. The O1s core-level spectrum of NCZ was divided into two peaks, one located at 531.2 eV corresponding to M–O bonds and the other centered at 533.2 eV associated with O–C=O.^[194]

Concerning the deconvoluted XPS spectra for Cu 2p in NCC, Figure C10a presents two noticeable doublets which were attributed to Cu $2p_{3/2}$ and Cu $2p_{1/2}$ of divalent Cu (II), individually, bearing splitting energy of approximately 19.5 eV.^[194] The lower BEs located at 935.4 and 937.4 eV were coupled with those positioned at higher BEs, 954.9 and 957.3 eV, and were associated with respective phases of CuO and $Cu_2(OH)_2CO_3$,^[192, 195] in line with XRD results (refer to Figure C6). Moreover, the shake-up satellite peak found at 944.3 eV was meanwhile ascribed to Cu $2p_{3/2}$. It is worth

noting that the Cu 2p spectrum of NCC/Ni-BDC was also analyzed (Figure C10b). The results displayed the movement of peaks to lower BEs with a difference of over 1.0 eV. In addition, the Ni 2p and Co 2p spectra were examined, disclosing similar observations. Analogous to NCZ/Ni-BDC, the NCC/Ni-BDC nanocomposite shifted to lower BEs in comparison with NCC, implying the strong interaction between the two components (NCC and Ni-BDC). As a result of the combination of two components, NCC/Ni-BDC experienced lower oxidation states and higher electron densities. Finally, the O 1s spectrum of NCC exhibited two identical peaks to those of NCZ, positioned at 531.2 and 533.3 eV related to M–O bonds and O–C=O.[194]



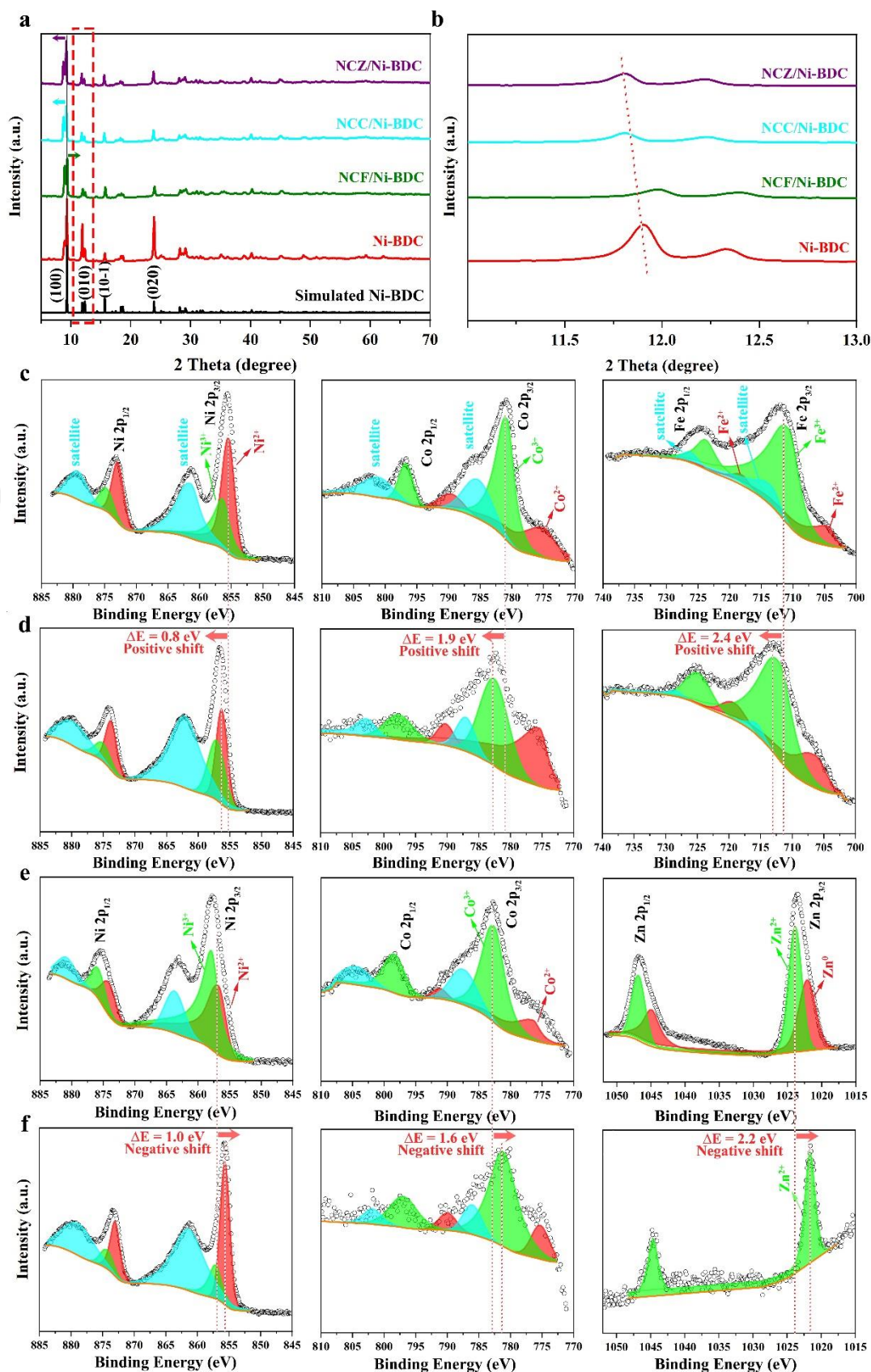


Figure 5. 2. Spectroscopic characterizations of selected samples. a) XRD patterns of blank Ni-BDC, NCF/Ni-BDC, NCC/Ni-BDC, and NCZ/Ni-BDC nanocomposites stripped off from NF, b) Shift of XRD (010) peaks for NCF/Ni-BDC, NCC/ Ni-BDC,

and NCZ/ Ni-BDC nanocomposites compared to simulated Ni-BDC pattern, c and d) XPS Ni 2p, Co 2p, and Fe 2p spectra for NCF and NCF/Ni-BDC, respectively, e and f) XPS Ni 2p, Co 2p, and Zn 2p spectra for NCZ and NCZ/Ni-BDC, respectively.

More insights into the structural information of the ternary oxide (NCM) and nanocomposites (NCM/Ni-BDC) were acquired via Fourier transform infrared spectroscopy (FT-IR). The left panel of Figure C11 depicts the FT-IR spectra conducted on NCM samples. Starting from the peaks detected at the region 3100–3600 cm^{-1} that were assigned to the O–H stretching vibrations of water molecules present in the samples.[196] The absorption bands that emerged at 2984 and 2902 cm^{-1} were indexed to C–H stretching vibrations originating from urea. Moreover, the existence of the H–OH functional groups has been witnessed by the appearance of peaks at $\sim 1512 \text{ cm}^{-1}$. [197] In addition, the bands centered at 1364 and 1044 cm^{-1} corroborated the presence of carbonates.[198] The respective transmittance peaks located at ~ 830 and $\sim 475 \text{ cm}^{-1}$ were associated with Co–O and Ni–O in the framework of ternary oxide.[198-200] Eventually, the appeared transmittance peaks at 687 cm^{-1} for NCM oxides were correlated with Fe–O, Cu–O, and Zn–O bonds, individually.[197]

The right panel of Figure C11 demonstrates the FT-IR spectra recorded for Ni-BDC and its derivative nanocomposites. The observed peaks at 3608 and 3423 cm^{-1} can be emanated from the stretching vibrations of O–H.[166, 201] The distinctive peaks positioned at 1374 and 1576 cm^{-1} were generated from the symmetric and asymmetric vibrations of –COO^- groups, respectively, verifying the presence of dicarboxylate linker in Ni-BDC.[202] The division of two modes manifested that the –COO^- group of 1,4-BDC is attached to Ni via a bidentate mode.[167] The absorption bands detected at 1524 cm^{-1} were ascribed to the stretching vibrations of para-aromatic CH groups.[166, 167, 203] In addition, the C–H bending vibrations were recognized via the IR bands recorded at the range of 750–880 cm^{-1} . Finally, the Ni–O vibration was identified through the bands in the region of 463 and 523 cm^{-1} . [203-205]

The microstructure morphology and phase composition of the Ni-BDC and the representative nanocomposites were further scrutinized by TEM and HR-TEM images. To exclude the effect of the NF template, samples were first scratched from the NF and then characterized. From TEM micrographs of pure Ni-BDC (Figure 5. 3a), the 2D nanosheet morphology (the lamellar sheet structure) is further confirmed as observed by SEM images. Unfortunately, the HR-TEM was not able to resolve the *d*-spacing of Ni-BDC 2D sheets. For this, the SAED image of Ni-BDC demonstrated a diffraction pattern

with well-defined spots along the [213] zone axis and evidently certified the structure of Ni-BDC (inset image of Figure 5. 3a). From the TEM photographs of NCF/Ni-BDC, the transparency of Ni-BDC nanosheet under incident electron beam is discernible on which numerous tiny nanoparticles are deposited (see Figure 5. 3b). We can observe a similar deposition of nanoparticles on nanosheets in the case of NCZ/Ni-BDC nanocomposite (Figure 5. 3c). The polycrystalline structure of nanoparticles on Ni-BDC sheets can be identified by the HR-TEM analysis. It can be claimed that both NCF and NCZ are composed of nanocrystallites < 20 nm in size.

The crystalline nanostructures in NCF/Ni-BDC were distinguished by their well-resolved lattice fringes with interplanar spacings of 0.228, 0.249, 0.294, and 0.25 nm corresponding to the crystalline planes of Ni(OH)_2 (221), $\text{Co}_2(\text{OH})_2\text{CO}_3$ (031), Fe_3O_4 (220), and Fe_2O_3 (110), individually (Figure 5. 3b: third image from left). Similarly, for the case of NCZ/Ni-BDC, clear crystal planes with a *d*-spacing of 0.234, 0.249, and 0.214 nm were assigned to the presence of ZnCo_2O_4 (222), CoCO_3 (006), and NiOOH (221), separately (Figure 5. 3c: third image from left). In addition, the high porosity of distributed nanoparticles can be substantiated by domains (orange dashed lines) of 5–10 nm in size. From an electrochemical point of view, this distinct mesoporous morphological feature is believed to be beneficial—in that, the electrolyte can reach easily every part of the sample bringing forth rapid ion/electron transfer, thereby leading to enhanced electrochemical reactivity.[206, 207] A HAADF-STEM associated EDS elemental mapping (Figure 5. 3d,e) manifested that the obtained NCF/Ni-BDC is composed of Ni, Co, Fe, C, and O elements, and NCZ/Ni-BDC nanocomposite consists of elements of Ni, Co, Zn, C, and O which for both samples, the elements are uniformly distributed in the representative batch. Finally, atomic force microscopy (AFM) revealed that a single nanosheet of Ni-BDC separated by ultrasonication has a typical thickness of ~3 nm and a much larger lateral size (Figure 5. 3f), corroborating the two-dimensionality of the Ni-BDC MOF array.

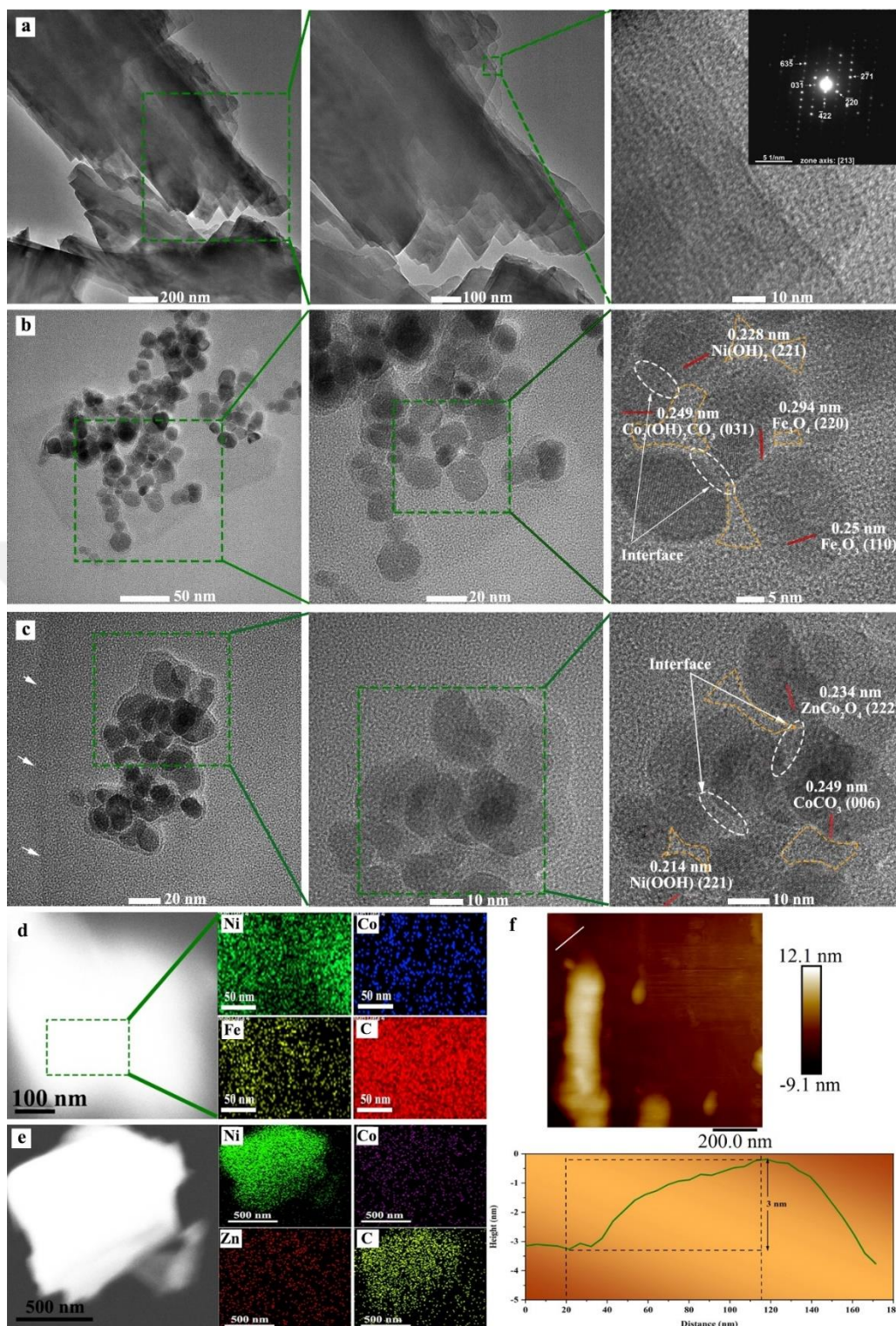


Figure 5.3. Morphological, structural, and microstructural characterizations of the selected sample. a) TEM photographs of blank Ni-BDC with different magnifications (inset: SAED image of Ni-BDC), b and c) TEM and HR-TEM images of NCF/Ni-BDC and NCZ/Ni-BDC, respectively; the first image from left shows the transparent Ni-BDC nanosheet decorated with ternary oxide nanoparticles, third image from left displays the lattice fringes of nanoparticle, white dotted circles show the interfaces and orange dotted lines shows the porosity between nanoparticles, d and e) HAADF-STEM image and the corresponding STEM-EDS mappings of NCF/Ni-BDC and NCZ/Ni-BDC, respectively, and f) AFM image and corresponding height profile of blank Ni-BDC.

5.3.2. *Electrocatalytic Activity of the Electrodes for the OER and HER*

The electrochemical aspects of the as-prepared catalysts were examined through a series of electrochemical measurements with a standard three-electrode configuration under ambient conditions in a 1.0 M KOH solution. Figure 5. 4a depicts the electrocatalytic OER activities of in-situ grown materials on NF substrate along with blank NF and commercial RuO₂ as a comparison. A small anodic peak was observed below 1.4 V vs RHE on the polarization curves of some samples which can be ascribed to the oxidation of Ni²⁺ to Ni³⁺ to form the active intermediate responsible for the OER.[208] For this, the inset figure demonstrates a better image of the corresponding potential of each catalyst at 10 mA cm⁻² current density. Besides, the current density at 50 mA cm⁻² was also delineated. It should be pointed out that the current densities were normalized to the geometric surface area of the substrate (0.5 cm × 1 cm). From the results, NCF/Ni-BDC electrode exhibits respective potentials of 1.35 and 1.68 V vs RHE to afford 10 and 50 mA cm⁻² current densities, respectively ($\eta^{10}_{\text{OER}} = 120$ mV and $\eta^{50}_{\text{OER}} = 450$ mV). We should highlight that sometimes it is very difficult to identify the OER overpotential because of the oxidation of the metal. To deal with this issue, chronopotentiometry at 10 mA cm⁻² (showing 1.43 V vs RHE) was performed for NCF/Ni-BDC which is discussed later. In addition, NCF delivers the 10 and 50 mA cm⁻² at $\eta^{10}_{\text{OER}} = 160$ mV and $\eta^{50}_{\text{OER}} = 350$ mV, individually. To compare the results with high-quality electrocatalysts, we have summarized the results of recent reports in Table C2.

It is noteworthy to mention that in the case of OER, the reaction kinetics—unlike HER—is completely different from one catalyst to another and highly pH-dependent. For instance, the onset overpotential of IrO₂/RuO₂ to initiate the reaction is lower compared to that of Ni-Fe, nonetheless, the Tafel slope is smaller for the latter one. This means that, while the driving force to start the reaction on IrO₂/RuO₂ is lower, the rate of charge transfer/electron transfer is lower than for the Ni-Fe system in alkaline media. Thus, people have adopted two critical parameters of overpotential at defined current density and Tafel slope to assess the value of electrocatalysts in OER.[8]

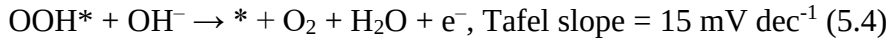
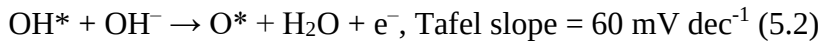
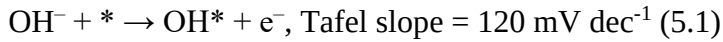
The OER performance of all as-fabricated samples is summarized in Table C3. By comparing the outcomes, it can be stated that electrodes containing Fe meaningfully outperform other electrodes containing Zn and Cu. Accordingly, from the OER performance point of view for both ternary oxide and nanocomposites the trend is as follows Fe > Zn > Cu. There is a common property occurring in all materials showing

good OER performance which is the presence of spinel oxides in their structure. To be specific and in parallel with XRD results, NCF and NCZ as well as their corresponding nanocomposites are composed of spinel oxides. According to crystal field theory[6], the transition metals in spinels can exhibit tetrahedral and octahedral coordinations, which result in different *d*-band splitting. The strong interaction between spinel bimetallic oxides with Ni-BDC MOF from one side and versatile valence states ($\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ in Fe_3O_4 and $\text{Co}^{2+} \rightarrow \text{Co}^{3+}$ in ZnCo_2O_4) of spinel oxides from the other side allowed us to modify the electronic structure of resulting hybrids for further optimization of the binding conditions between the intermediates and reactants during OER. But NCF and its relevant nanocomposite stand out in terms of their OER performance. The above-written discussions showed the presence of layered $\text{Ni}(\text{OH})_2$ in these two samples (refer to the schematic image in Figure C1).

The layered structure-type oxides are categorized as the layered double hydroxides (LDH), and this family is usually cobalt- and nickel-based compounds on account of their remarkable OER activity. Subbaraman et al.[209] reported a systematic investigation on the 3d transition-metals (Ni, Co, Fe, Mn) hydr(oxy)oxide for OER and found the following trend for these compounds, ($\text{Ni} > \text{Co} > \text{Fe} > \text{Mn}$). The excellent catalytic activity appertained to the optimal binding strength between Ni and OH. Besides, Corrigan[210] demonstrated that a trace amount of Fe impurity would substantially increase the OER activity of NiOOH . They concluded that a further increase in Fe content resulted in even higher performance. The overpotential, η^{10}_{OER} observed in our work illustrated the same results. Among the ternary oxides, NCF (containing both iron oxide and $\text{Ni}(\text{OH})_2$) has the lowest value, followed by NCZ (containing only NiOOH) and NCC (neither iron oxide nor $\text{Ni}(\text{OH})_2$). The OER performance for the nanocomposites is further elevated as coupling metal oxides/hydroxides with 2D MOFs endows the resulting hybrid with enormous active sites as a result of metal sites being highly exposed to electrolyte ions for use in catalytic reactions.

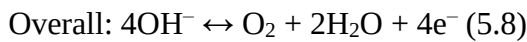
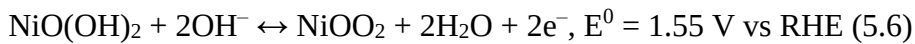
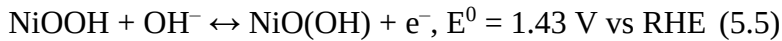
To study the electrochemical kinetic behavior, the Tafel slopes were calculated and plotted. As mentioned before, the Tafel slope is derived from polarization curves and measures how much potential is required to generate a tenfold current density.[80] To ensure the authenticity of the comparison, it is recommended to determine all Tafel slopes within a similar current density region. The results can be visualized in Figure 5. 4b. Similar to OER experiments, Fe-containing materials possess more facile kinetics in terms of the Tafel slope. From Figure 5. 4b, NCF/Ni-BDC and NCF displayed the lowest

Tafel slopes of 35.1 and 39.5 mV dec⁻¹. Based upon the previous reports, the proposed four-step OER process with relevant Tafel slopes is as follows[211]:



In the preceding reactions, * represents a catalytic site, and OH*, O*, and OOH* are the adsorbed intermediates.[188] From the calculated values, the rate-determining step for NCF/Ni-BDC is between 40–15 mV dec⁻¹, suggesting that the rate-determining step for this sample might be the formation of OOH* or desorption of O₂ which is a sign of favorable kinetics. Similarly, the small Tafel slope (39.5 mV dec⁻¹) of NCF implies that its OER kinetics conforms to OOH* formation. The rate-controlling step of NCZ/Ni-BDC and NCZ (Tafel slope = 60.2 and 68.7 mV dec⁻¹, respectively) however, follows the second step in the OER process (O* formation).[212] Figure 5. 4c illustrates the relation between the Tafel slope and overpotential at 10 mA cm⁻² of the investigated electrocatalysts, demonstrating the superiority of NCF, NCZ, and their relevant nanocomposites.

For the Ni-based catalysts, the above-mentioned reactions can be modified as[213-215]:



From these reactions, the first and second steps are reversible, whereas the third step is fast and irreversible, determining the overall rate of the process. Highly OER active catalysts are utilized to alleviate the kinetic barrier of the third step which is the case for NCF/Ni-BDC and NCF in this work. In general, NiO₆ inside Ni-BDC can be oxidized to NiO₆/NiOOH species as active sites to enhance the oxidation of OH⁻ to O₂. Moreover, on the basis of XPS analysis, NCF/Ni-BDC nanocomposite contains metallic atoms with higher oxidation states and hence lower electron densities. Experimentally, Fe, Ni, and Co atoms within NCF/Ni-BDC draw more electrons compared to NCF and thereby are better electron acceptors.[179] It must be borne in mind that Fe-based oxides/hydroxides can appreciably promote the OER performance once they are used together with Ni- and Co-based oxides/hydroxides which is the case for NCF/Ni-BDC and NCF electrodes.

Concerning this, the XRD pattern of NCF (Figure C6) and HR-TEM micrographs of NCF/Ni-BDC (Figure 5. 3b: third image from left) substantiated the coexistence of oxides/hydroxides. The identified crystalline interfaces for NCF/Ni-BDC nanocomposite are Ni(OH)₂ (221) with Co₂(OH)₂CO₃ (031) as well as spinel ferrite Fe₃O₄ (220) with Fe₂O₃ (110). According to previous studies[212] on Co-Fe binary metal oxide, the interface formation between different oxides may minimize the activation barrier for the generation of intermediate. Concerning NCF and NCF/Ni-BDC electrodes, the existence of interfaces most likely alleviated the kinetic of OOH* formation to accelerate O₂ generation.

In addition to the linear equation of Tafel discussed in the electrochemical measurements section, the Tafel slope can be inversely proportional to the charge transfer coefficient (α) following the relation expressed below[6]:

$$b = \frac{2.303RT}{\alpha F} \quad (5.9)$$

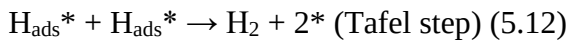
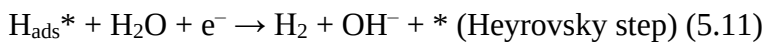
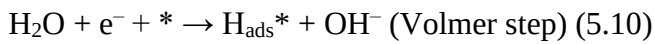
In this relation, b , R , T , and F are respectively indicative of Tafel slope (V dec⁻¹), the universal gas constant (8.314 J mol⁻¹ K⁻¹), absolute temperature (298 K), and Faraday constant (96485 A s mol⁻¹). In this context, the higher the charge transfer ability of a catalyst, the smaller the Tafel slope. The computed charge transfer coefficient of each sample was tabulated in Table C3. In accordance with this table, NCF/Ni-BDC, NCF, and NCZ/Ni-BDC with respective α values of 1.68, 1.49, and 0.98 have the largest capacity for charge transfer, manifesting their good electrocatalytic kinetics. Comparing the charge transfer ability of commercial RuO₂ (0.54) with investigated materials in this study indicated that as-prepared catalysts are much more competent at lower current densities and comparable to the RuO₂ at higher current densities (see overpotential values at 50 mA cm⁻² in Table C3).

To implement the overall water splitting with bifunctional catalysts, HER is another equally significant half-reaction as OER. Figure 5. 4d portrays the HER performance of investigated samples together with commercial 20% Pt/C and blank NF. As expected, state-of-the-art Pt/C@NF electrode and blank NF, respectively, featured the lowest and highest overpotential at 10 mA cm⁻² (η^{10}_{HER} = 61 and 314 mV). Among all as-prepared materials, NCZ/Ni-BDC exhibited the lowest HER overpotential, η^{10}_{HER} = 170 mV. In this sense, Ni-BDC, NCF, NCC, NCZ, NCF/Ni-BDC, and NCC/Ni-BDC, with respective η^{10}_{HER} values of 268, 231, 183, 236, 215, and 215 showed inferior HER activity compared to NCZ/Ni-BDC. Interestingly, NCC stands out among the ternary mixed oxide catalysts

owing to the incorporation of a Cu source. Cu, a transition metal element from d-block displays high thermal and electrical conductivities, and its oxides and hydroxides have been widely studied for both OER and HER. What is more, all three Cu-based species (CuO, Cu(OH)₂, and Cu₂(OH)₂CO₃) detected in the NCC sample (see Figure C6) have been known as excellent H₂-production cocatalysts.[216-219]

To be consistent with the comparison basis of OER performance, η^{50}_{HER} was evaluated for each sample and tabulated in Table C3. Comparison of HER performance of fabricated electrodes at 50 mA cm⁻² with that of commercial Pt/C@NF further elucidates the value of prepared catalysts. To this end, Pt/C@NF with $\eta^{50}_{\text{HER}} = 214$ mV is still the best HER catalyst within the scope of this study, followed by NCZ/Ni-BDC@NF (351 mV), NCC@NF (366 mV), and NCF/Ni-BDC@NF (373 mV). At this point, it should be emphasized that coupling ternary mixed oxides with 2D Ni-BDC enhanced the HER performance of hybrids excluding the NCC/Ni-BDC electrode. The reason for this phenomenon can be pertained to lower active sites which can be explained by electroactive surface area. Finally, Table C2 presents the HER activity of NF-based MOFs and/or metal oxide electrocatalysts. With reference to this table, the best-performing nanocomposite in this work is comparable to other MOF-derived documented catalysts such as Fe-Ni@NC-CNT ($\eta^{10}_{\text{HER}} = 202$ mV)[16], Ni@NC-800 ($\eta^{10}_{\text{HER}} = 205$ mV),[19] and NiFe-MOF ($\eta^{10}_{\text{HER}} = 134$ mV).[213]

In alkaline media, the HER kinetics is explained by the adsorption/desorption of hydrogen atoms/molecular hydrogen through either Volmer-Heyrovsky or Volmer-Tafel mechanisms, reaction[220]:



where, * stands for the available active sites, and H_{ads}* represents the atomic hydrogen at the active site. Ideally, one can infer the HER mechanism through Tafel plots derived from LSV curves. The experimental studies have already proven the corresponding Tafel slope values for each step. For this, if the reaction mechanism is controlled by the Volmer step, it requires a Tafel slope of ~120 mV dec⁻¹. In contrast, if the rate-controlling step of the HER is the Heyrovsky or Tafel reaction, a much smaller Tafel slope of about 40 mV dec⁻¹ or 30 mV dec⁻¹ will be uncovered. However, it should be stressed that the Tafel slope can be altered by several elements such as applied potential, the heavy presence of adsorbates, and mass transport in porous structures.

Experimentally, it has been revealed that the Pt electrode is controlled by the Tafel path with a slope of 30 mV dec^{-1} . Nevertheless, increasing applied potential leads to saturation of the catalyst surface with adsorbed hydrogen atoms, resulting in accelerated atom–atom recombination. Consequently, the rate-limiting step was flipped to a Volmer path with a Tafel slope of 120 mV dec^{-1} . [220] In this work, the Pt/C electrode showed a Tafel slope of 96.4 mV dec^{-1} , verifying its validity with literature in alkaline conditions and approving its rate-limiting step, Volmer.

All as-developed materials—except for NF—displayed a Tafel slope value beyond 120 mV dec^{-1} (see Figure 5. 4e), indicating that they are controlled by the hydrogen atom adsorption step at the active sites. Still, among examined catalysts, NCZ/Ni-BDC exhibited a lower Tafel slope ($137.2 \text{ mV dec}^{-1}$) compared to other samples which confirms more facilitated kinetics of hydrogen adsorption at the active sites. Another important parameter which is an index to determine the intrinsic electrocatalytic activity of materials at the reversible overpotential ($\eta = 0$) is called exchange current density (j^0), [7] and it can be obtained by extrapolating the linear portion of the Tafel plot. The exchange current density is more often used as an activity parameter for the HER than for the OER. The HER kinetics is facile regardless of the defined overpotential of the catalyst. In this sense, it can be stated that all reported catalysts have quite identical HER kinetics. This means that the exchange current density is directly correlated to the onset overpotential in the HER, [8] the higher the j^0 , the more active the catalyst. Looking at the exchange current densities of the examined catalysts in Table C3 reveals that Pt/C ($j^0 = 1.08 \text{ mA cm}^{-2}$) is the most active HER catalyst and NF substrate ($j^0 = 0.017 \text{ mA cm}^{-2}$) is the least active HER catalyst in this study. In addition, in accordance with LSV results, NCZ/Ni-BDC ($j^0 = 0.78 \text{ mA cm}^{-2}$) is the best HER catalyst among as-synthesized materials, followed by NCC ($j^0 = 0.69 \text{ mA cm}^{-2}$).

For decades Ni-based alloys have been found as potential HER catalysts when combined with other transition metals. For this, Raj et al. [221] prepared several binary Ni-based alloys on mild-steel substrates for the HER using electrodeposition techniques. They found that NiZn alloy is one of the very best HER electrocatalysts. Moreover, Wang et al. [222] reported that the addition of Zn to NiMo alloy could promote the valence states of metallic Ni and Mo and thereby significantly enhance the current density to ten- and fifteen-fold compared to pure Ni and NiMo alloy, individually. The best HER catalyst, NCZ/Ni-BDC, demonstrated significant enhancement compared to its components, Ni-BDC and NCZ. On the basis of XPS results, Ni, Co, and Zn atoms in NCZ/Ni-BDC

nanocomposite have lower oxidation states (= higher electron density) when compared to NCZ. This means that hydrogen atoms, H^+ , can easily adsorb at the active sites and facilitate the Volmer step. Another possibility is that NiO_6 inside MOF can be partially reduced to form Ni/NiO_6 interface at the cathode. On such interface, the OH^- generated by H_2O splitting could preferentially attach to a NiO_6 site at the interface due to strong electrostatic affinity to the locally positively charged Ni^{2+} species, while nearby $Ni/Co/Zn$ sites would facilitate H^+ adsorption and thus the Volmer process, imparting synergistic HER catalytic activity.[223] Furthermore, as shown in Figure 5. 3c (third image from left), the synergistic interface effect between crystalline phases in NCZ/Ni-BDC can be evinced. The partial reduction of metal oxide/hydroxides to metals can accelerate the proton adsorption and subsequent recombination to H_2 .[212] Finally, Figure 5. 4f represents the relation between Tafel slope and overpotential, suggesting that commercial Pt/C and NCZ/Ni-BDC are the best catalysts for the hydrogen production. In the meantime, we evaluated the OER and HER performances of NCZ' (with $Zn(NO_3)_2 \cdot 6H_2O$ as zinc source) and NCZ'/Ni-BDC under the same conditions. Due to their poor performance (Figure C12) comparing to their counterparts, we decided not to conduct further experiments.

The electrochemical impedance spectroscopy (EIS) measurements were investigated at 0 V vs RHE to study the intrinsic charge transfer capacity of the catalysts. Figure 5. 4g illustrates the resulting Nyquist plots, curve-fitted with an equivalent circuit model to gain the charge transfer resistance data. The equivalent circuit model for porous electrodes is represented as an inset of Figure 5. 4g. In this model, R_e , stands for electrolyte resistance, while $R_p/CPE1$ and R_{ct} (charge transfer resistance)/CPE2 are related to the porosity of the electrode and the interface between catalyst and electrolyte, respectively. The capacitive element can be replaced by a constant-phase element (CPE) due to the complex nature of the interfacial reaction.

Nyquist plots reveal a semicircle shape at high frequencies followed by a straight line at low frequencies, which in some plots tends to bend (NCZ/Ni-BDC and NCF/Ni-BDC). At high frequencies, the AC signal cannot penetrate the bottom of the pore because of the IR drop. On the other hand, at low frequencies, the AC signal can penetrate throughout the pore and the measured capacitance corresponds to the total capacitance of the pore walls. What is more, at low frequencies, capacitance is the total capacitance of the porous and flat surface of the electrode. In practical applications, diffusion consists of a finite-length linear layer, where the diffusion layer corresponds to the thickness of the layer.

Among the two types of finite-length diffusion (transmissive and reflective boundaries), transmissive boundaries are associated with steady-state concentration gradients in membranes, in which a semicircle is obtained because a DC can flow.[224] Keeping these in mind, according to the Nyquist plots (Figure 5. 4g), a transmissive boundary is shown because the arc region is included and the sample is strictly capacitive, especially for the high-performance NCF/Ni-BDC and NCZ/Ni-BDC catalysts. On the contrary, for the NCZ, NCF, and Ni-BDC ones, the reflective boundary diffusion could be considered, in which the mass transfer impedance displays a quite straight line at 45° at high frequencies because the penetration length of the AC signal is smaller than the layer thickness, consequently the imaginary part goes to infinity as the constant current cannot flow in the system.

The intrinsic behavior of the catalysts on the kinetics of electrochemical processes could be interpreted from the data. The estimated values obtained from the EIS simulations by the ZView software are listed in Table C4. Based on the results, the nanocomposite materials remarkably decrease surface resistance. In this sense, for the best-performing NCF/Ni-BDC and NCZ/Ni-BDC catalysts, respectively, the interface charge transfer resistance (R_{ct}) decreased to 116.3 and 126.9 Ω compared to the Ni-BDC (494.9 Ω), resulting in a significant improvement in electron transport. Undoubtedly, nanocomposite materials have more efficient electron transfer between the active sites of electrode and electrolyte ions.

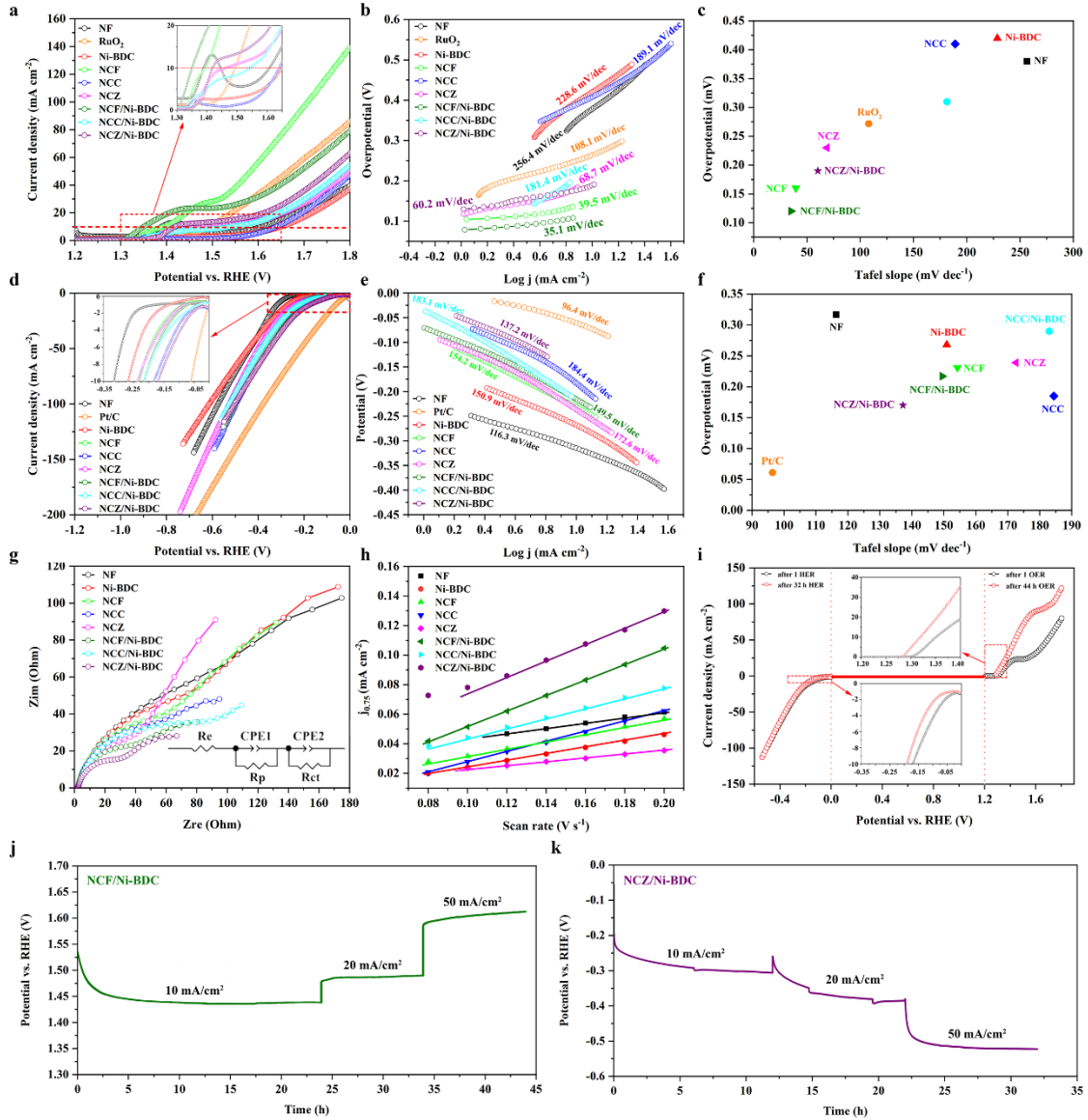


Figure 5.4. Electrochemical oxygen evolution and hydrogen evolution performances. a and d) OER and HER polarization curves of various catalyst samples: red and blue dotted lines display 10 and 50 mA cm⁻², respectively, b and e) OER and HER Tafel plots obtained by polarization curves, respectively, c and f) Comparison of the overpotential at a current density of 10 mA cm⁻² and Tafel slope on various OER and HER samples, respectively, g) EIS spectra recorded at 0 V vs RHE, h) Capacitive current density vs scan rate curves for ECSA measurements, i) OER and HER polarization curves before and after long-term durability measurements for best-performing OER (NCF/Ni-BDC) and HER (NCZ/Ni-BDC) samples, and j and k) Long-term durability tests of NCF/Ni-BDC and NCZ/Ni-BDC for OER and HER, respectively at 10, 20, and 50 mA cm⁻².

To further realize the remarkable performance of the two best materials toward OER (NCF/Ni-BDC) and HER (NCZ/Ni-BDC), the electrochemical surface area (ECSAs) of all samples were compared by estimating the double-layer capacitance (C_{dl}) through cyclic voltammetry (CV) recorded at various scan rates within the potential window of

0.7–0.8 V vs RHE (Figure C13). In this context, ECSA can be obtained through the following equation [225]:

$$\text{ECSA} = C_{\text{dl}}/C_{\text{NF}} \quad (5.13)$$

where C_{NF} is a C_{dl} value of NF substrate in 1.0 M KOH.[15] Founded on the foregoing relation, ECSA and C_{dl} have direct relation, meaning that the higher the C_{dl} the higher the ECSA.[8]

Figure 5. 4h illustrates the C_{dl} values for all samples that the following order can be drawn into attention: NCZ (0.121 mF cm⁻²; ECSA = 0.65) < NF (0.184 mF cm⁻²; ECSA = 1.0) < Ni-BDC (0.22 mF cm⁻²; ECSA = 1.2) < NCF (0.244 mF cm⁻²; ECSA = 1.32) < NCC/Ni-BDC (0.328 mF cm⁻²; ECSA = 1.78) < NCC (0.344 mF cm⁻²; ECSA = 1.87) < NCZ/Ni-BDC (0.483 mF cm⁻²; ECSA = 2.62) < NCF/Ni-BDC (0.525 mF cm⁻²; ECSA = 2.85). Interestingly, the electroactive surface area for NCZ/Ni-BDC and NCF/Ni-BDC have enlarged over two-fold compared to bare Ni-BDC. Therefore, the best nanocomposite catalysts offer the largest exposed electroactive surface areas, confirming their enhanced electrocatalytic activity.[226]

Metal oxides/hydroxides are active catalytic centers for OER, HER, and overall water splitting; however, they usually show compromised catalytic performance owing to limited exposed metal active sites. In contrast, MOF material has inherent molecular metal centers, as potential active sites for electrocatalysis[213]. As mentioned in previous discussions, coupling metal oxides/hydroxides with 2D MOFs endows the resulting hybrid with enormous active sites as a result of metal sites being highly exposed to electrolyte ions for use in catalytic reactions. This was certified by a respective two-fold and four-fold increase of electrochemically active surface measured by using the double-layer capacitance of the composite electrodes, NCF/Ni-BDC (0.525 mF cm⁻²) and NCZ/Ni-BDC (0.483 mF cm⁻²) compared with their ternary oxide electrodes NCF (0.244 mF cm⁻²) and NCZ (0.121 mF cm⁻²). Moreover, as shown in Figure 1a, the layered structure of Ni-BDC allows for better storage and diffusion of electrolyte solution. Yet, it is accepted that ECSA alone, is not an indicator to ascertain the activity of the electrode since ECSA is a quantitative factor to measure the active sites which means the quality of the active sites is equally important.[86] To support the ECSA results, we determined the Brunauer–Emmett–Teller (BET) specific surface areas of Ni-BDC, NCF/Ni-BDC, and NCZ/Ni-BDC, which were found to be 3.27, 6.91, and 4.77 m²/g. Considering the low BET surface area of the samples which could be attributed to the closely packed lamellar morphology of the catalysts, their high performance can be stemmed from their

in-situ growth on the 3D microscopic porous framework of NF. The N₂ adsorption-desorption isotherms can be found in Figure C14.

The stability and durability of the samples are other critical factors to appraise their performance for practical applications. The stability of the best-performing samples for OER and HER was tested using chronoamperometric experiments at 10, 20, and 50 mA cm⁻². As shown in Figure 5. 4j the OER potential of NCF/Ni-BDC at 10, 20, and 50 mA cm⁻² are fixed at 1.43, 1.47, and 1.59 V vs RHE, demonstrating outstanding long-term durability under 1.0 M KOH. Figure 5. 4i depicts LSV curves toward OER for NCF/Ni-BDC before and after nearly 45 h continuous OER operation. Surprisingly, we observed a significant enhancement in OER performance in terms of both overpotential at a fixed current and overall current density within the entire OER region. From the results before and after long-term durability experiments, η^{10}_{OER} dropped from 120 mV to 80 mV and η^{50}_{OER} declined from 450 mV to 200 mV. Besides, before the longevity test, the overall current density reached 80 mA cm⁻² at 1.8 V vs RHE, however, the post-OER stability sample generated above 120 mA cm⁻² at the same potential. Similarly, the HER long-term durability for NCZ/Ni-BDC was conducted in 1.0 M KOH. Unlike OER, NCZ/Ni-BDC exhibited decent HER durability. From Figure 5. 4i, the LSV curve after 32 h HER operation uncovered that η^{10}_{HER} and η^{50}_{HER} increased from 170 to 190 mV and from 350 to 360 mV, respectively, verifying its relative durability. From Figure 5. 4k, the chronoamperometry curve displayed the respective potential of 300, 385, and 520 mV at the fixed current density of 10, 20, and 50 mA cm⁻².

5.3.3. *Post-Electrocatalysis Characterization*

To investigate any type of alterations following the OER, HER, and their relevant prolonged water oxidation/reduction after roughly 45 and 32 h in alkaline conditions, we further characterized the catalysts. The microstructural studies for the high-performance OER (NCF and NCF/Ni-BDC) and HER (NCC and NCZ/Ni-BDC) samples were demonstrated via SEM-coupled EDS elemental mappings (Figures C15 and C16). Evidently, the samples after exposure to one HER did not display significant changes. Therefore, the morphology of HER samples remained largely intact and from the topographical image displayed in inset images of Figure C15b and d, no detachment was observed. In contrast, the samples after exposure to one OER demonstrated some alterations. From the SEM image of NCF (Figure C15a), large crystalline features are

noticeable which can be attributed to hundreds of nanorods joined to each other in an alkaline medium. The micrograph of NCF/Ni-BDC exhibited vertically aligned sheets like those before the OER reaction, but thicker (see Figure C15c). Furthermore, the EDS elemental mappings confirmed the presence of all elements after electrocatalysis (Figure C16). Finally, XPS spectra were analyzed and assigned to distinctive species (refer to Figure C17).

The high-resolution SEM image of the anodic catalyst after the long-term OER durability test can be seen in Figure 5. 5a in which the lamellar structure changed to a great extent; heavily starched layers (Figure 5. 1g) transformed to separate bundles of layers. The difference between the morphology of NCF/Ni-BDC before and after OER stability is significant in that the porosity within the structure increased tremendously (comparison between the inset image of Figure 5. 5a and top-view SEM image of Figure C3b) and led to an extremely low overpotential at 50 mA cm^{-2} (200 mV). It can be observed that the porous space between each bundle is beyond several hundred micrometers. The major disadvantage of 2D MOF-derivative materials is regarded to be their potent inclination to aggregate which drastically declines their electrocatalytic activity.[179] However, the inset image of Figure 5. 5a shows that the aggregation of NCF/Ni-BDC has been significantly mitigated. This can be attributed to the crystal structure transformation in line with the reaction (14); from hydrated $\text{Ni}_3(\text{OH})_2(\text{tp})_2(\text{H}_2\text{O})_4$ within the triclinic system to anhydrous $\text{Ni}_2(\text{OH})_2\text{tp}$ (shown in Figure 5. 5i) within the monoclinic system (space group $\text{C2}/m$) which is supported by the XRD pattern of NCF/Ni-BDC after OER durability test (see Figure 5. 5c).[167] In addition, from the TEM images, the original shape of nanoparticles cannot be found. Figure 5. 5g shows the HR-TEM images of the post-OER anode in which the formation of amorphous phases (delineated by a white dashed line) such as FeOOH is evident which is due likely to partial degradation of Fe_2O_3 with lattice fringe of 0.25 nm corresponding to the crystalline plane of (110). Eventually, the HR-TEM image shown in Figure C18a disclosed the existence of NiOOH . It must be noted that NiOOH as the actual catalytic active site for OER can be created during electrochemical activation following the oxidation of $\text{Ni}(\text{OH})_2$. [86, 227]



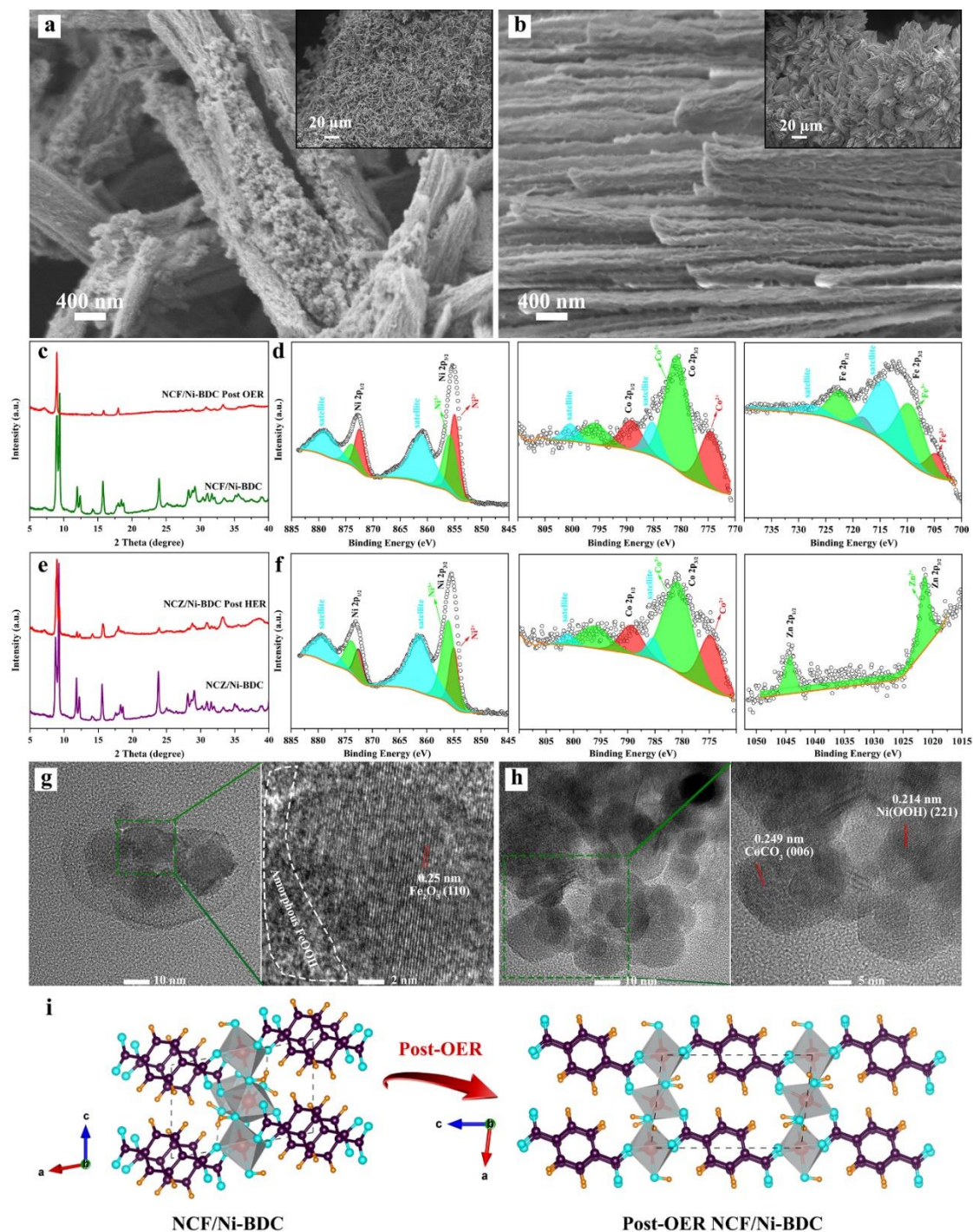
On the flip side, the cathodic catalyst remained largely unchanged both morphologically and structurally. Figure 5. 5e depicts the XRD pattern of the post-HER catalyst, reflecting all diffraction peaks matching with the XRD pattern of the fresh

sample. Moreover, the SEM photograph shown in Figure 5. 5b illustrated no microstructural and morphological changes after 32 h of continuous HER experiment. Furthermore, the TEM and HR-TEM analyses (Figure 5. 5h) confirmed the presence of embedded nanoparticles with high crystallinity, identical to the fresh catalyst, NCZ/Ni-BDC (see Figure C18b). With this in mind, it can be inferred that partial detachment of the catalyst from its substrate resulted in a slightly higher overpotential after 32 h. The compositional survey and chemical states for the post-OER and HER catalysts were implemented. Concerning the NCF/Ni-BDC after long-term OER (see Figure 5. 5d), the high-resolution XPS core-level spectra for Ni 2p revealed the two doublets corresponding to Ni^{2+} and Ni^{3+} and meaningfully shifted to small BEs compared to the fresh sample (refer to Figure 5. 2d), implying that low-priced nickel would be oxidized to high-priced nickel in the reaction process.[171] The same situation occurred for Co 2p and Fe 2p for which both 2+ and 3+ states appeared and shifted to small BEs. In addition, the comparison of Fe^{2+} before and after prolonged OER discloses a drastic intensity decrease which can be the coverage effect of the amorphous phases such as the FeOOH layer on the surface.[228] Finally, the XPS analysis of Ni 2p, Co 2p, and Zn 2p (shown in Figure 5. 5f) slightly shifted in the direction of small BEs as opposed to the fresh sample (Figure 5. 2f), manifesting the formation of new species and in turn change in the electronic configuration of metal atoms on the surface. It can be concluded that the cathodic side did not go under severe change and no metal Ni, Co, and Zn were formed during the reduction process.

We need to clarify the complicated nature of the post-OER XPS results. A thorough investigation of the OER dynamics of Ni-Fe mixed by Görlin et al.[229] suggested that Ni-based catalysts undergo a noticeable redox state between 2+ and 3+/4+ following OER electrolysis, corroborated by both X-ray absorption spectroscopy (XAS) and operando differential electrochemical mass spectrometry (DEMS) based faradaic efficiency data. However, they stated the story differs when Fe comes into the picture. The presence of Fe in the active mixed Ni-Fe catalysts stabilizes the low-valent Ni centers. Moreover, pure Fe likewise did not display a change in its redox state. From the redox state point of view, concerning XPS results for NCF/Ni-BDC, our work is in line with the study conducted by Görlin et al.[229]

To further prove the stability of the catalysts after OER and HER longevity tests, the amount of dissolved metallic atoms was recorded via inductively coupled plasma-mass spectrometry (ICP-MS). As shown in Table C5, only a trace amount of elements are

present in the electrolyte, meaning that the most of elements are preserved after long-term OER/HER durability.



Given the remarkable OER performance of NCF/Ni-BDC and the great HER performance of NCZ/Ni-BDC in 1.0 M KOH solution, we further assembled a couple-electrode cell to examine its competence in overall water splitting. For comparison, NF || NF, Pt/C (cathode) || RuO₂ (anode), Ni-BDC || Ni-BDC, and NCC (cathode) || NCF (anode) electrolyzers were likewise constructed and tested under the same conditions (see Figure 5. 6a). From Figure 5. 6b, NCZ/Ni-BDC || NCF/Ni-BDC delivered 10 mA cm⁻² at the applied cell voltage of 1.58 V which is 20 mV lower than that of benchmark Pt/C || RuO₂. Even though Pt/C is the best HER material in this work (compared to as-prepared catalysts), the presence of NCF/Ni-BDC as the best-performing OER sample (much better than RuO₂) controls the two-electrode cell performance. Besides, the performance of assembled couple is comparable to the recently documented couple electrode cells (Table C2). In addition, NF || NF exhibited an insignificant performance and was not able to generate 10 mA cm⁻² within the applied potential window (1.2–1.8 V), demonstrating the negligible impact of NF substrate on the electrocatalytic performance of the samples. Moreover, Ni-BDC || Ni-BDC and NCC || NCF couples afforded 10 mA cm⁻² at the respective cell voltage of 1.77 and 1.65 V. The EIS experiments were carried out on the assembled electrolyzers at the cell potential of 0 V (fitted with the same equivalent circuit model of Figure 5. 4g) and the results confirmed the significant difference between NCZ/Ni-BDC || NCF/Ni-BDC with other electrolyzers, showing appreciably lower resistance (refer to Figure 5. 6c). The related fitted values are listed in Table C4. Based on the results, for a couple-electrode cell, the Nyquist plots displayed more reflective boundary diffusion almost at all frequencies. For the Ni-BDC || Ni-BDC and NCC || NCF couples, the plots did not include the complete arc region and the samples were not utterly capacitive. On the other hand, for the NCZ/Ni-BDC || NCF/Ni-BDC system, the interface charge transfer resistance (R_{ct}) decreased to 423 Ω compared to the Ni-BDC || Ni-BDC ($37.8 \times 10^9 \Omega$) and NCC || NCF (2818 Ω), resulting in a significant improvement in electron transport for the nanocomposite system.

To analyze the practicality of the NCZ/Ni-BDC || NCF/Ni-BDC in terms of durability and stability, the current density of 20 mA cm⁻² was applied to the couple-electrode cell for 20 h. The chronopotentiometry curves in Figure 5. 6d discloses that NCZ/Ni-BDC || NCF/Ni-BDC couple is quite stable after 20 h in a 1.0 M KOH medium, exhibiting a negligible increase in the required potential to reach 20 mA cm⁻² throughout the whole 20 h. Furthermore, the amount of H₂ and O₂ from the overall water splitting

(without using any membrane to separate the gas products), operated at 20 mA cm⁻² for 150 min was quantified by a gas chromatograph (GC), shown in Figure 5. 6e. The faradaic efficiencies for both HER and OER reactions were calculated in accordance with eq. 5. 15 and compared to the theoretical data[230] (refer to Figure 5. 6f).

$$FE = \frac{n_{exp}}{Q/ZF} \quad (5.15)$$

In the preceding formula, n_{exp} refers to the number of moles of H₂ or O₂ experimentally produced at constant current density (e.g., 20 mA cm⁻²), Q (C) denotes the total amount of charge, Z number of transferred electrons (i.e., in HER, $Z = 2$ and in OER, $Z = 4$), and F is the Faraday's constant (96485 C mol⁻¹). It was found that HER and OER have respectively the efficiencies of 100 and 85 %, demonstrating great potential for electrolytic hydrogen production.

To learn the plausible reasons for the 15% loss in O₂ faradaic efficiency, we should take the reaction dynamics of the OER process into account which was described by Görlin et al.[229] According to their operando DEMS analysis which was applied to quantitatively calculate the O₂ faradaic efficiency during a cyclic voltammetric OER scan, the total efficiency is a result of two components. i) the faradaic charge which accounts for the number of oxidizing species depleted for water oxidation (O₂ formation), ii) the oxidation charge which accounts for the number of redox species needed for oxidation-state changes of the metal centers. Based on this study which was conducted on Ni-based, Ni-Fe mixed, and Fe-based catalysts, the low faradaic O₂ evolution for Ni-based materials was ascribed to the 1-electron Ni^{2+/3+} redox charge process. They further stated that the addition of Fe into Ni-catalysts could stabilize the redox properties of Ni centers, leading to higher O₂ faradaic efficiencies in Ni-Fe mixed materials. From this, we can conclude that a 15% loss in OER faradaic efficiency for NCF/Ni-BDC can be originated from the redox process during water electrolysis of metal centers especially Ni which is the most dominant metal in this framework relative to Fe and Co. Still, it is not possible to claim the precise oxidation states of Ni, Fe, and Co in this material after electrolysis process which contributed to the faradaic efficiency loss.

5.4.Mechanism Discussion

First, the hierarchical growth of NCM/Ni-BDC@NF brought about the synergy between the three components. Multiple metal centers created synergy in NCM oxides, and their peculiar morphology strengthened the synergistic effect between 2D layers of

Ni-BDC and NCM. Besides, the 3D open structure of NF with a large specific surface area improved the mass and electron transfer of the in-situ grown materials. Second, the crystal/crystal interfaces formed within the 3D structure of NCM promoted the adsorption/desorption of the intermediates. Third, on the anode side, NiO₆ inside Ni-BDC can be oxidized to NiO₆/NiOOH species as active sites to enhance the oxidation of OH⁻ to O₂. Moreover, the strong interactions between Ni-BDC and NCF could decrease the electron density and generate Ni, Co, and Fe with higher oxidation states which greatly boosted the intrinsic OER activity of NCF/Ni-BDC. Fourth, on the cathode side, NiO₆ inside MOF can be partially reduced to form Ni/NiO₆ interface. On such interface, the OH⁻ generated by H₂O splitting could preferentially attach to a NiO₆ site at the interface due to strong electrostatic affinity to the locally positively charged Ni²⁺ species, while nearby Ni/Co/Zn sites would facilitate H⁺ adsorption. Furthermore, the interaction between Ni-BDC and NCZ generated Ni, Co, and Zn with higher electron densities and encouraged the electrolytic HER of NCZ/Ni-BDC. In addition to the above-written aspects, the layered structure of Ni-BDC facilitated the storage and diffusion of electrolyte solution to deposited NCM nanoparticles. Last, but not least, coupling metal oxides/hydroxides with 2D MOFs endows the resulting hybrid with enormous active sites as a result of metal sites being highly exposed to electrolyte ions for use in catalytic reactions. This was certified by an increase in electrochemical active surface measured by using the double-layer capacitance of the composite electrodes. Altogether, all the mentioned features of fabricated hybrids are responsible for remarkable OER, HER, and overall water splitting.

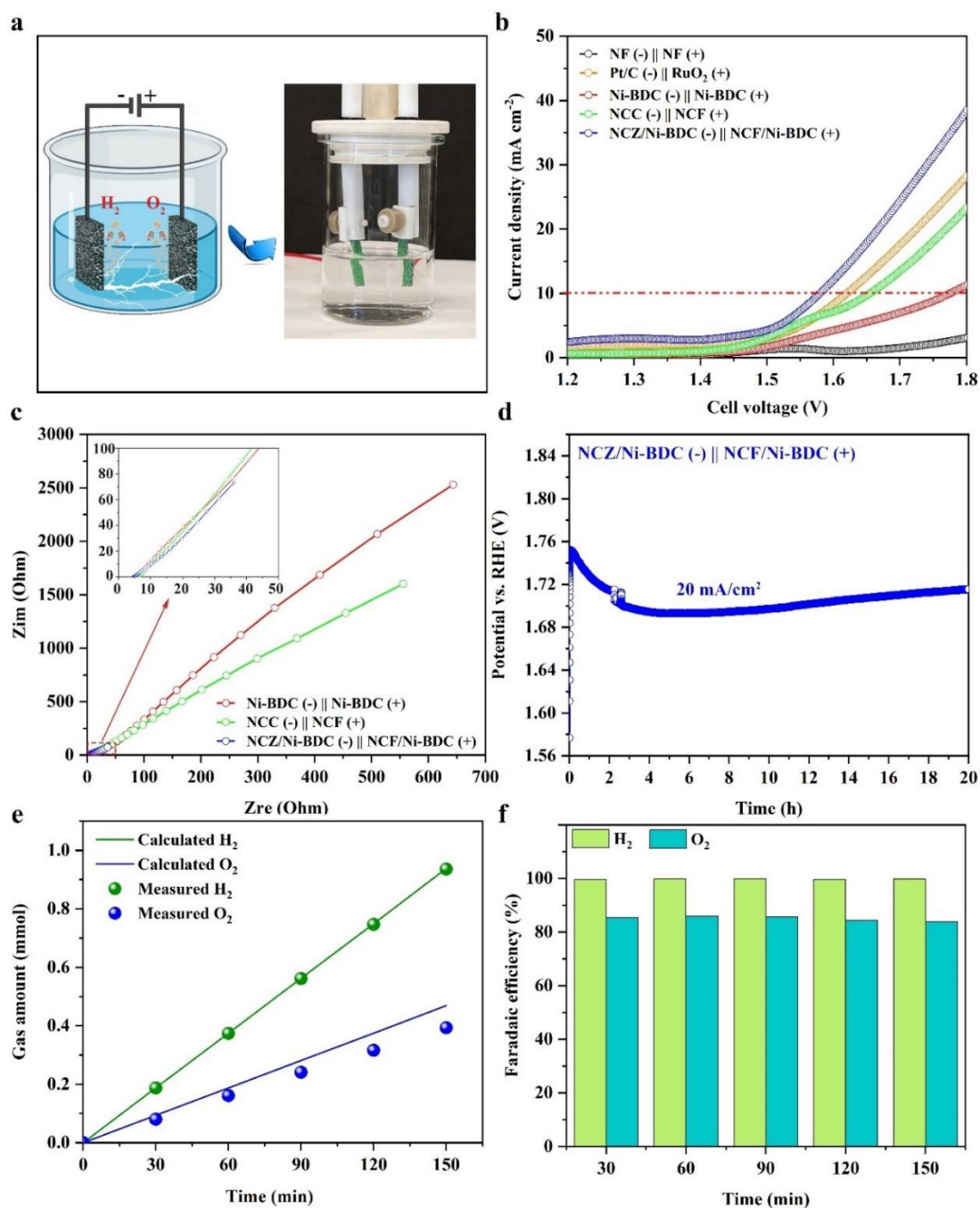


Figure 5. 6. Electrochemical activity of various electrolyzers for overall water splitting in 1.0 M KOH. a) Schematic and a digital photograph of two-electrode cell used in this work, b) Polarization curves of various catalysts used as the cathode (-) and anode (+) in a two-electrode cell, c) EIS spectra recorded at the cell potential of 0 V for constructed electrolyzers, d) Long-term durability test of the best-performing NCZ/Ni-BDC || NCF/Ni-BDC couple at the constant current density of $20\ mA\ cm^{-2}$, e) Electrochemical efficiency of overall water splitting for H_2 and O_2 production at $j = 20\ mA\ cm^{-2}$ on NCZ/Ni-BDC || NCF/Ni-BDC electrodes, and f) Quantification of the Faraday efficiency of water electrolysis for NCZ/Ni-BDC || NCF/Ni-BDC electrolyzer.

5.5.CONCLUSIONS

In conclusion, we successfully fabricated Ni-Co-*M* oxide (*M* = Fe, Cu, Zn) [NC*M*: *M* = F, C, Z] /Ni-BDC MOF@NF nanocomposites on the conductive 3D porous backbone of NF via a simple solvothermal process. Compared to Ni-BDC and ternary oxide, NCF/Ni-BDC and NCZ/Ni-BDC were endowed with higher electrochemically active surface area. The oxidation states of the metallic atoms in both nanocomposites were manipulated in favor of OER and HER. In this context, NCF/Ni-BDC demanded respective potential of 1.35 and 1.68 V vs RHE to deliver 10 and 50 mA cm⁻² toward OER. At the same time, NCZ/Ni-BDC yielded 10 and 50 mA cm⁻² at the respective overpotential of 170 and 350 mV toward HER in alkaline solutions. When used for overall water splitting, the NCZ/Ni-BDC || NCF/Ni-BDC couple electrode only required a cell voltage of 1.58 V to achieve the current density of 10 mA cm⁻², outperforming the benchmark electrode couple of Pt/C || RuO₂. The NCF/Ni-BDC nanocomposite was decorated with multiple crystalline interfaces such as Ni(OH)₂ (221) with Co₂(OH)₂CO₃ (031) as well as spinel ferrite Fe₃O₄ (220) with Fe₂O₃ (110) which endowed the anode with remarkable performance for the adsorption of OH⁻ ions to facilitate the oxygen-evolving process. On the cathodic side, the Ni-BDC nanosheets were decorated with ZnCo₂O₄ (222) and CoCO₃ (006) which in turn led to lower oxidation states that expedited the H⁺ ions adsorption. Finally, the as-prepared couple electrolyzer demonstrated excellent durability at an applied cell potential of 20 mA cm⁻² for 20 h. As a whole, the synergy between multiple factors including the hierarchical architecture of Ni-BDC nanosheets and ternary oxide nanoparticles on the 3D open framework of the conductive substrate, modulation of electronic structure, formation of multiple metal/metal oxide interfaces, and creation of abundant active sites culminated in the design of highly efficient catalysts toward overall water splitting. The faradaic efficiencies of the NCZ/Ni-BDC || NCF/Ni-BDC electrolyzer were obtained by quantifying the H₂ and O₂ via a gas chromatograph and were estimated to be 100 and 85 %, respectively.

CHAPTER 6

NiMo/CoMoO₄ HETEROSTRUCTURE WITH CONFINED OXYGEN VACANCY FOR ACTIVE AND DURABLE ALKALINE HYDROGEN EVOLUTION REACTION

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6.1.Introduction

Metal molybdates, a significant class of inorganic materials, have possible uses in various areas, such as catalysis, magnetic applications, humidity sensing, photoluminescence, and energy storage.[231-233] CoMoO₄, a member of the metal molybdates family, has been found to enjoy compelling properties including nontoxicity, unique crystal structure, multiple valence states, and ability to reversibly store small ions, which makes it a favorable choice as an electrode material.[231, 232] However, the poor electrical conductivity of CoMoO₄ and the limited number of active sites are the reasons for its unsatisfactory HER performance in alkaline media. To improve the electrocatalytic character of CoMoO₄ for the HER, various research methods have been employed to boost electron transfer and increase the number of active sites. These methods include modifying the electronic structure of CoMoO₄ by introducing element dopants, heterostructure engineering, controlling the crystal facets, and creating oxygen vacancies.[35, 234]

In this study, a heterostructure composed of a metallic-like component (NiMo alloy) and an oxide (CoMoO₄) was fabricated directly on a NF substrate. The NiMo/CoMoO₄@NF reached 10 mA cm⁻² at a low overpotential of 102 mV in a 1.0 M KOH solution.

In general, the superior activity of the NiMo/CoMoO₄ catalyst toward HER could be attributed to one or more of the following factors: i) the large number of active sites correlated with electrochemically active surface area (ECSA) as well as specific surface area coming from Brunauer, Emmett and Teller (BET) analysis; both ECSA and BET surface area grew three-fold larger compared to CoMoO₄, ii) a proper regulation of binding ability of intermediates (OH* and H*) with active sites; metallic-like NiMo has adsorption affinity toward H* while oxygen vacancy confined-CoMoO₄ has adsorption affinity toward OH*, leading to higher intrinsic activity compared to single components, iii) an appropriate interface engineering can enhance electron transfer and redistribution; for this, unique atomic coordination at the interface of NiMo NPs and CoMoO₄ can significantly affect the electrocatalytic HER. Once NiMo is combined with CoMoO₄, the interface of the heterostructure is expected to experience an electronic redistribution due to the varying electronegativities of the atoms involved (3.44 for O atom, 1.91 for Ni, 1.88 for Co, and 2.16 for Mo).

6.2. EXPERIMENTAL SECTION

6.2.1. Catalyst Preparation

6.2.1.1. Materials

Polyvinylpyrrolidone (PVP, Sigma-Aldrich), nickel chloride hexahydrate (NiCl₂·6H₂O, Sigma-Aldrich, 99.9% trace metals basis), sodium molybdate dihydrate [Na₂MoO₄·2H₂O, Sigma-Aldrich, ACS reagent, ≥ 99%], sodium borohydride (NaBH₄, Sigma-Aldrich), and cobalt nitrate hexahydrate [Co(NO₃)₂·6H₂O, Sigma-Aldrich, 99.999% trace metal basis] were purchased and used without any prior treatment.

6.2.1.2. Synthesis of NiMo Nanoparticles

The method used to synthesize NiMo alloy NPs followed a previously reported surfactant-aided co-reduction process,[235] with some minor modifications. To briefly summarize, 1g of PVP was dissolved in 50 mL of deionized (DI) water to make a clear, colorless solution. Then, 356 mg of NiCl₂·6H₂O (1.5 mmol) and 120 mg of Na₂MoO₄·2H₂O (0.5 mmol) were added to the PVP-containing solution and dissolved via vigorous stirring—a nominal composition of 3:1 for Ni/Mo. After 30 min, 200 mg of NaBH₄ was quickly added into the above mixture solution and the reaction mixture was stirred vigorously until the formation of bubbles stopped. The resulting black suspension was rinsed with DI water and pure ethanol repeatedly and then vacuum dried at 100 °C for 24 h. For better understanding the crystallinity of obtained NiMo NPs, the ground powder was transferred into an alumina crucible and then inserted into a homemade tubular quartz tube. The tube was then placed in a tubular furnace and heated under an Ar atmosphere at 550 °C for 3 h.

6.2.1.3. Synthesis of NiMo/CoMoO₄@NF

The commercial NF (1.5 cm × 3 cm) was treated under ultrasonication with 2.0 M HCl solution, acetone, deionized water, and ethanol each for 10 min to remove contaminants such as oxide from the NF surface, and dried by exposing it to the open air. For the fabrication of CoMoO₄ on NF, 2 mmol of Co(NO₃)₂·6H₂O and 2 mmol of Na₂MoO₄·2H₂O were dissolved in 40 mL DI water. The ingredients were mixed by stirring at room temperature until a clear, deep red solution was formed. A specified quantity of already prepared powder of NiMo NPs (20 wt. %) was added to the solution mixture and stirred for 60 min. The solution was subjected to ultrasonic vibrations for an additional 60 min. The prepared mixture was then poured into a 50 mL Teflon-lined

stainless-steel autoclave and the previously cleaned NF was added to it. The autoclave was tightly sealed and placed in an oven, where it was kept at 140 °C for 6 h. After being allowed to cool down to room temperature naturally, the Co-Mo precursor coated on NF was washed with DI water and pure ethanol, and then vacuum dried overnight at 60 °C. Finally, the NF coated with Co-Mo precursor/NiMo was put into an alumina crucible, and the same calcination step was performed for 3 h at 550 °C under Ar flow. The NiMo/CoMoO₄ on NF was obtained after the sample cooled to room temperature under Ar flow (see schematic illustration in Figure 6. 1a). The CoMoO₄ on the NF substrate was synthesized with the same process without using NiMo addition to the solution prior to the hydrothermal step.

6.2.1.4. Preparation of Pt/C@NF

In brief, 1 mg commercial 20% Pt/C was ultrasonically dispersed in a solution of pure ethanol (300 µL) and DI water (200 µL) for 30 min. Afterward, 10 µL Nafion solution was added and sonicated for another 30 min to gain a homogeneous ink solution. The prepared ink was pipetted onto a piece of NF to obtain a mass loading of approximately 1 mg cm⁻².

6.2.2. Materials Characterization

The crystal phase and purity of the products were analyzed by XRD, Rigaku Mini Flex 600, Cu K α radiation, $\lambda = 1.5418$ Å). The morphology was investigated by an FE-SEM; Zeiss Ultra Plus equipped with an EDS detector (Bruker Xflash 5010, 123 eV spectral resolution). The microstructure, SAED, and lattice fringes were further studied by (HR-TEM; Thermo Scientific Talos F200S 200 kV). In addition, HAADF-STEM images and the associated EDS-STEM mappings were taken on a microscope (Hitachi HF5000 200 kV (S)TEM, working at HR mode). The surface composition and oxidation states were obtained by (XPS, Thermo Scientific K-Alpha with an Al K α monochromator source, 1486.6 eV). All XPS spectra were corrected according to the binding energy (BE) of C 1s = 284.50 eV. The vibrational modes of molecules were monitored by Raman spectroscopy (Raman microscope, RENISHAW INVIA, 532 nm excitation laser source). The functional groups were identified by Fourier transform-infrared spectroscopy (FT-IR, JASCO 6800 full vacuum & FT-IR microscope). X-Band (9.65 GHz) electron paramagnetic resonance (EPR) measurements were performed at room temperature with Bruker EMX Nano. The offset in the magnetic field and the exact g-factors in X-band

measurements were determined with a polycrystalline DPPH (2-diphenyl-1-picrylhydrazyl) reference sample with a well-known g-factor ($g = 2.0036$). The BET specific surface area was determined through N₂ adsorption-desorption isotherms (BET, Micromeritics ASAP 2010). Finally, inductively coupled plasma-mass spectrometry (ICP-MS) Agilent 7700x was employed to check the possibility of Pt spring—the counter electrode—dissolution in the alkaline conditions after the post-stability test.

6.2.3. *Electrochemical Characterization*

All electrochemical experiments were performed by an AutoLab Potentiostat Galvanostat (PGSTAT302N, made in the Netherlands) in a standard three-electrode system in an alkaline solution (1.0 M KOH). A reversible hydrogen electrode (RHE; HydroFlex) was used as the reference electrode, and a Pt spring was employed as the counter electrode. The catalysts grown on NF (0.5 cm × 1 cm) were utilized as working electrodes. The linear sweep voltammetry (LSV) curves were recorded in the HER potential region (0 to −1 V) at a scan rate of 5 mV s^{−1}. The HER overpotentials were considered at current densities of 10 and 50 mA cm^{−2}. The recorded LSV curves were then replotted to receive Tafel plots. The ECSA was acquired through the double layer capacitance (C_{dl}) with respect to the CV measured at various scan rates of 0.02, 0.04, 0.06, 0.08, 0.1, and 0.12 V s^{−1} across the potential window from 0.75 to 0.85 V vs RHE. The turnover frequency (TOF) was determined with a consistent interval of 100 mV, within a defined overpotential range of 100–500 mV. The long-term HER stability was performed through a chronopotentiometry test at an applied current density of 30 mA cm^{−2} for 30 h. The electrochemical impedance spectroscopy (EIS) measurements were performed at 0.0 V vs RHE over a frequency region of 100 kHz to 0.1 Hz. To better study HER kinetics, the EIS experiments were carried out at 100–200 mV vs RHE at a regular interval of 10 mV. All the electrochemical data were presented without iR correction as the iR drop was calculated to be 11.7 Ω. The obtained value was introduced to the electrochemical measurements, and it had almost no impact on the results. Finally, hydrogen gas production was detected and quantified using a gas chromatograph (7820A, GC-System, Agilent) equipped with a thermal conductivity detector (TCD). The experiment was conducted in a tightly sealed cell to ensure accuracy, and a three-electrode configuration system was employed, consistent with the electrochemical characterizations.

6.3.RESULTS AND DISCUSSION

6.3.1. Chemical Studies

The XRD characterization was employed to examine the phase structure of NiMo NPs, CoMoO₄, and NiMo/CoMoO₄. As shown in Figure 6. 1b, NiMo before heat treatment shows only one broad peak at around $2\theta = 45^\circ$, demonstrating its amorphous nature which is common for NiMo alloys with various compositions.[235, 236] On the flip side, we can see a highly crystalline phase after heat treatment at 550 °C. It is noticed that the representative peaks of Ni in NiMo shifted to the lower 2θ values relative to the XRD pattern of reference Ni (ICSD code no. 260172), indicating the formation of an alloy structure between Ni and Mo (marked by ♦).[235] Meanwhile, we can infer the enlargement of interlayer spacing with reference to Bragg's law.[237] It is noteworthy to mention that extremely low-intensity peaks (marked by ●) also appeared which correspond to the MoO₂ phase. With this in mind, Mo deficiency is expected in NiMo which will be further discussed later. In addition, the XRD patterns of CoMoO₄ and NiMo/CoMoO₄ can be visualized in Figure 6. 1c. Almost all the characteristic peaks are well assigned to the β -CoMoO₄ (ICSD code no. 760022). Finally, two weak peaks emerged at around $2\theta = 14^\circ$ (marked by *) and 35.7° (marked by ■) which were attributed to α -CoMoO₄ and MoO₃, respectively. It can be concluded that the designed heterostructure is almost a single-phase β -CoMoO₄.

At this point, it might be useful to note that CoMoO₄ occurs in multiple phases: the low-temperature α -phase, the high-temperature β -phase, the high-pressure hp-phase, and the hydrate.[238] The α -phase CoMoO₄ resides in the monoclinic space group $C2/m$ (No.12). The β -phase crystallizes in the same space group but is subtly different from the α -phase due to the tetrahedral coordination of the Mo⁶⁺ ions as opposed to an octahedral environment observed for the α -phase. The calcination conducted on the Co-Mo precursor induces the phase transition from α -phase to β -phase.[239] Knowing that there are plenty of experimental publications discussing the difference between these two phases, still the transition between $\alpha \rightarrow \beta$ at room temperature after some time makes it a bit challenging to claim whether the prepared materials are metastable or not. To avoid any confusion, we repeated the XRD analysis on the prepared materials after four months and did not observe any phase transition. Therefore, it can be concluded that the β -phase

CoMoO₄ fabricated in this study is metastable in which the transition is kinetically hindered.

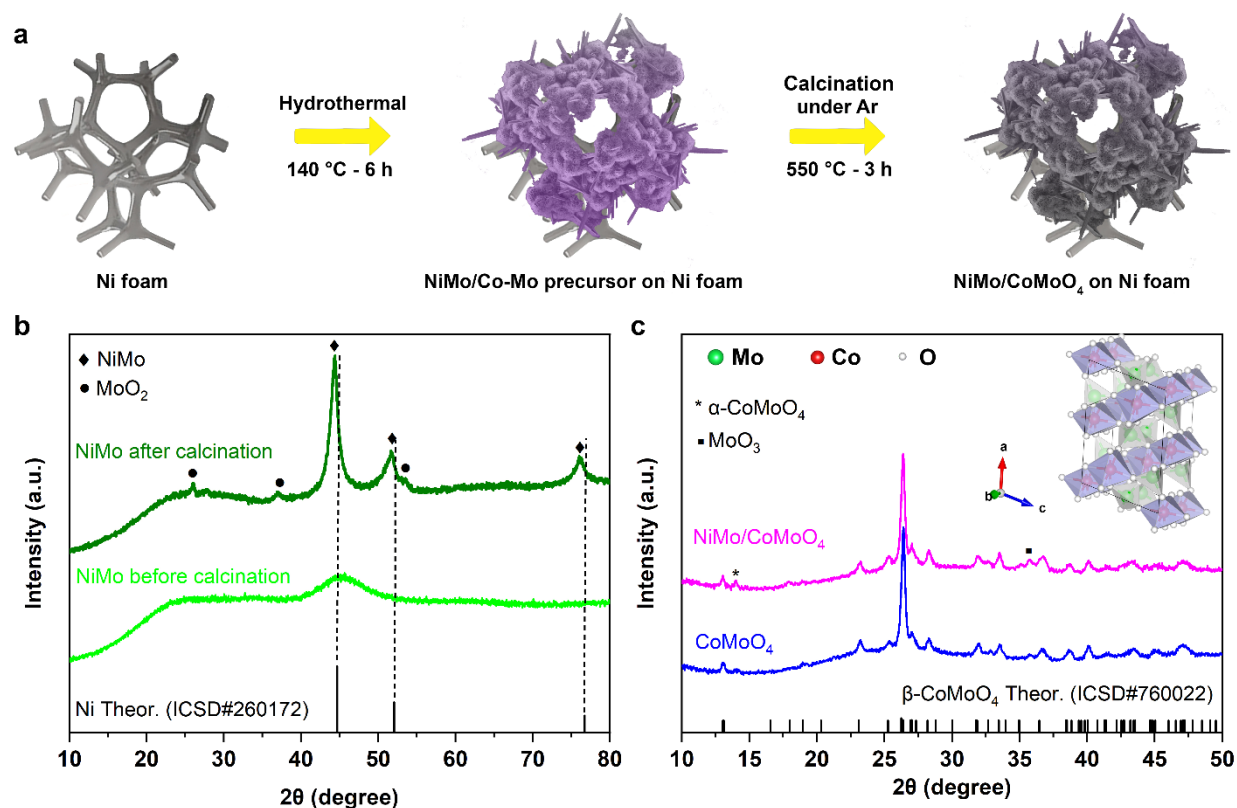


Figure 6. 1. a) Schematic illustration of preparation procedure of NiMo/CoMoO₄ heterostructure, b) XRD patterns of NiMo NPs before and after heat treatment at 550 °C under Ar, and c) XRD patterns of pristine β -CoMoO₄ and NiMo/CoMoO₄ (inset: crystal structure of CoMoO₄).

The morphology of the catalysts was characterized by FE-SEM. The SEM image of NiMo before the calcination step is demonstrated in Figure 6. 2a which shows highly agglomerated NPs with an estimated size of < 20 nm. Meanwhile, both SEM micrographs of NiMo before and after heat treatment can be viewed in Figure D1. However, the size of these sponge-like agglomerated NPs cannot be easily determined. The EDS elemental mapping and the corresponding elemental spectrum display an even distribution of Ni and Mo over the entire batch of the sample (refer to Figure D2a). The atomic ratio of Ni/Mo was received to be 4:1 from various spots of the sample batch. It should be considered that the nominal composition of Ni/Mo from initial precursors was 3:1. Nonetheless, the XRD patterns confirmed the presence of MoO₂ besides NiMo alloy, implying Mo deficiency.

The SEM photographs of pristine CoMoO₄ and the composite, NiMo/CoMoO₄, on NF can be observed in Figure 6. 2b,c. The SEM image of pristine CoMoO₄ showcases two distinct morphologies of interwoven nanorods and nanoflowers (high magnification image in the inset of Figure 6. 2b,c) which are evenly distributed on the backbone of NF (refer to Figure D3). The building blocks of both structures are nanosheets joined to one another either in a one-dimensional (1D) orientation to construct the nanorods or in a circular orientation to develop the nanoflowers. The average thickness of nanosheets can vary from 20 to 60 nm. Similar structures can be seen from the SEM micrographs of NiMo/CoMoO₄ grown on NF, except that the size of nanoflowers became smaller compared with pristine CoMoO₄ and most of the long nanorods transformed into much shorter pieces (shown in Figure 6. 2c). The nanoflowers in NiMo/CoMoO₄ wind around the broken rods, creating a porous area on the substrate. The porous structure can provide a large surface area for electrochemical reactions and accelerate the transportation of electrolyte ions, elevating the rate of alkaline HER.[233] The EDS mapping of CoMoO₄ and NiMo/CoMoO₄ shown in Figure D2b,c confirmed the presence of their constituent elements and their uniform dispersion over the NF template.

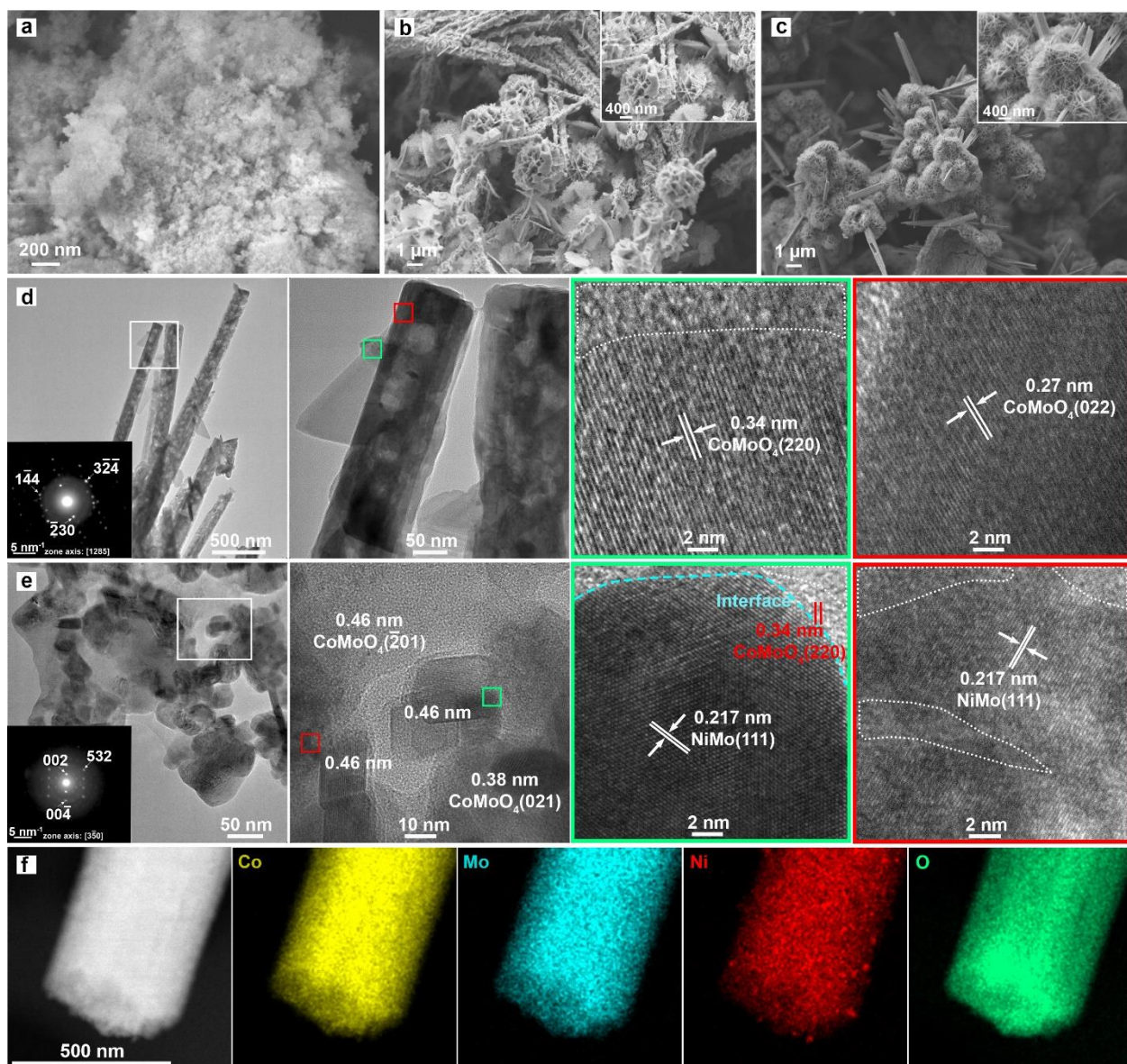
To further interpret the crystal structure, morphology, and defects of the as-obtained materials, TEM, HR-TEM, SAED, and HAADF-STEM were utilized. As can be seen from Figure D4a the well-dispersed NPs of NiMo before calcination are less than 10 nm in size. The low crystallinity of NPs is verified by the SAED image which is in accordance with the amorphous XRD pattern (shown in Figure 6. 1b). The TEM photographs of NiMo after heat treatment, on the other hand, illustrate a dramatic change in terms of crystallinity, the amorphous NPs transformed into highly crystalline particles with an average size of ~ 13 nm (see Figure D4b). The HR-TEM image of heat-treated NiMo exhibits clear lattice fringes with an interplanar distance (d) of 0.217 nm which can be assigned to partial Mo incorporation into the crystal structure of Ni. It is worthy of mention that the d-spacing of Ni(111) is 0.202 nm which can be enlarged with the introduction of a heteroatom like Mo. The result accords with the XRD pattern, noticeable peak shift in the direction of lower 2θ values (refer to XRD interpretation). A similar observation was documented by Yang et al.[235]

Figure 6. 2d depicts the TEM images of pristine CoMoO₄ scratched off from NF. CoMoO₄ consists of smooth 1D nanorods with an average diameter of ~ 135 nm and a length of up to micrometers. The HR-TEM photographs exhibit two lattice spacings of

0.34 nm (green square) and 0.27 nm (red square) which can be well indexed to (220) and (022) planes of monoclinic CoMoO₄. The blurry lattice fringes shown in Figure 6. 2d (3rd image from left to right, shown with the enclosed white dotted area) demonstrate the existence of atomic structure distortion on the edges of the nanorods which might be originated from the oxygen atom deficiencies.[53] The TEM micrographs of NiMo/CoMoO₄ can be visualized in Figure 6. 2e which are mostly composed of nanosheets. The interplanar spacings of 0.46 and 0.38 nm are consistent with the respective crystalline planes of CoMoO₄($\bar{2}01$) and CoMoO₄(021). Interestingly, two distinguishable lattice fringes with d-spacings of 0.217 nm were found which can be attributed to the presence of NiMo NPs in the hybrid. To clarify this, metallic Ni(111) possesses a d-spacing of 0.202 nm. Once a solid solution between Ni and Mo is created, the resulting interplanar spacing enlarges from 0.202 to 0.217 nm. It must be highlighted that there is a tight interface between NiMo NPs with CoMoO₄ nanosheets, forming a heterostructure (blue line shown in Figure 6. 2e, 3rd image from left to right) to encourage the charge transfer. Meanwhile, the structure distortion can be discerned in Figure 6. 2e (3rd and 4th images from left to right, shown with the enclosed white dotted area), stemming from oxygen vacancies. More importantly, the oxygen deficiencies are located both on the surface and internal structure of NiMo/CoMoO₄, presenting higher defect concentration compared to pristine CoMoO₄, as evidenced in similar studies.[53] The observation could be attributed to the formation of oxygen bridging between two components through Ni–O–Co and/or Ni–O–Mo which will be clarified in more detail later. The inset images of Figure 6. 2d,e illustrate the SAED patterns of both samples of CoMoO₄ and NiMo/CoMoO₄ along the zone axes [1285] and [3 $\bar{5}$ 0], individually, verifying the formation of monoclinic CoMoO₄ structure. Finally, the HAADF-STEM image taken from NiMo/CoMoO₄ revealed Co, Mo, Ni, and O elements are dispersed evenly on the nanorod (shown in Figure 6. 2f).

XPS was utilized to get further insight into the surface chemistry and oxidation states of the prepared catalysts. The broad scan survey spectra verify the existence of expected elements in each sample (Figure 6. 3a, 1st panel from left to right). For the NiMo sample (depicted in Figure D5), Mo 3d spectrum displays two sets of doublets one at lower binding energy (BEs), 229.5 and 233.2 eV, and the other pair at higher BE, 231.5 and 234.8 eV. According to the literature, the former pair belongs to Mo(IV) and the latter pair corresponds to Mo(VI).[235, 236] In addition, Figure D5 shows XPS spectra for Ni

2p composed of two doublets of 2p_{1/2} and 2p_{3/2} as well as their satellite peaks which were perfectly fitted to Ni(II) and Ni(III).^[240] Moreover, the O 1s XPS spectra demonstrate three peaks, indicating oxidized species on the surface.



For pristine CoMoO₄, the deconvolution of the Co 2p region disclosed two main doublet pairs at 781.78, 797.58 eV and 783.88, 799.68 eV alongside their satellites corresponding to Co 2p_{3/2} and Co 2p_{1/2}, indicating the oxidation states of Co(II) and Co(III).[240, 241] The core level Mo 3d XPS spectrum for CoMoO₄ exhibited Mo(IV) at BEs centered at ca. 231.38 and 234.6 eV as well as Mo(VI) at ca. 233.2 and 236.28 eV (Figure 6. 3a).[234]

It is pronounced that the observed XPS spectra of Co 2p and Mo 3d for the NiMo/CoMoO₄ sample (Figure 6. 3b) slightly shifted to higher BEs—blueshift—compared with pristine CoMoO₄, indicating that the electron density of CoMoO₄ was adjusted with the addition of NiMo. This phenomenon confirms there was an electron transfer between two constituent components in the hybrid catalyst, from Co and/or Mo sites to Ni sites through oxygen bridging Ni–O–Co and/or Ni–O–Mo, resulting in lower electron density in Co and higher electron density in Ni sites. The deconvoluted Ni 2p spectrum NiMo/CoMoO₄ revealed that the two oxidation states of Ni(II) and Ni(III) are present in the hybrid sample, compared with NiMo, the BEs shifted to lower values. This finding confirms the electron transfer from CoMoO₄ to NiMo in the hybrid catalyst. The atomic proportion of both Mo and Co decreases in the hybrid catalyst (6.01% for Mo and 3.21% for Co) compared to pristine CoMoO₄ (8.57% for Mo and 6.91% for Co), further substantiating the electron transfer within the components via oxygen bonding.[232, 242-244]

To quantify the concentration of oxygen vacancies in pristine CoMoO₄ and the hybrid NiMo/CoMoO₄, the O 1s spectra for both samples were fitted. The emerged three peaks for CoMoO₄ at BEs of ca. 531.28, 532.28, and 533.76 eV were ascribed to the metal–oxygen bonding or lattice oxygen (O_{latt}), the representative peak of oxygen vacancy (O_v), and adsorbed hydroxyl groups (O_{ads}) on the surface, respectively.[53] The three peaks of O 1s for the hybrid catalyst appeared at a bit lower BEs. The ratio of O_v/O_{latt} was estimated for these two materials to be 0.69 for pristine CoMoO₄ and 1.84 for NiMo/CoMoO₄, implying a significant increase in the oxygen vacancy content on the surface after coupling CoMoO₄ and NiMo under heat treatment. With this concept, the engineered oxygen vacancy-confined NiMo/CoMoO₄ heterostructure is expected to be a good catalyst for the adsorption of water molecules and subsequently hydrogen reduction.

The structural changes between pristine CoMoO₄ and NiMo/CoMoO₄ were inspected by Raman spectroscopy (Figure 6. 3c). Six characteristic peaks were found in both

samples. The sharpest peak located at 938 cm⁻¹ denotes the symmetric stretching mode of Mo–O.[245, 246] The peaks situated at 874 and 814 cm⁻¹ represent asymmetric stretching vibrations of oxygen in O–Mo–O.[53] The band at 698 cm⁻¹ was assigned to the symmetric stretching of Co–O–Mo.[245, 246] The bands positioned at 367 and 328 cm⁻¹ correspond to symmetric torsional vibrations of O–Mo–O.[53, 245] For the NiMo/CoMoO₄ hybrid, the Raman shifting and peak broadening were observed (Raman shift in Figure D6a), suggesting that original lattice symmetry of CoMoO₄ was distorted which could be attributed to the oxygen defects, inducing disordered surface.[247]

FT-IR further substantiated the hybridization nature of NiMo/CoMoO₄. Figure 6. 3d illustrates the FT-IR spectra for CoMoO₄ and NiMo/CoMoO₄. The absorption bands at 925 and 780 cm⁻¹ denote stretching vibration modes of the O–Mo–O bond.[248-250] The peaks at 694 and 580 cm⁻¹ were attributed to the vibrations of the Co–O–Mo and Co–O groups, respectively.[250, 251] The band that appeared around 400 cm⁻¹ was assigned to the Mo–O and CoO₆ groups of CoMoO₄. [251] For the NiMo/CoMoO₄ hybrid, all the infrared signals match with those of pristine CoMoO₄ sample, however, the hybrid sample exhibits a slight redshift (shown in Figure D6b) around 500–750 cm⁻¹ which suggests that there might be some possible interactions between NiMo and CoMoO₄. [250] Besides, this region which is an indication of metal–oxygen vibration can be altered by the formation of oxygen defects. The oxygen deficiencies formed in the vicinity of Co–O may weaken the bond strength, giving rise to metal oxide stretching bands shifting to lower wavenumbers.[252]

The X-band EPR measurements were exploited to supply meaningful indications for the generation of oxygen defects within the pristine CoMoO₄ and NiMo/CoMoO₄ hybrid. Figure 6. 3e displays that both samples have paramagnetic defect centers and CoMoO₄ has two distinct EPR signals at $g = 2.4217$ and $g = 6.377$. It has been observed that the g factor can originate from the existence of Co ions associated with ionized oxygen vacancies. Moreover, the resonance intensity peak of the hybrid sample is much higher than that of pristine CoMoO₄, meaning that the metal (Ni/Mo)–oxygen formation masked the emergence of oxygen vacancy defect signals. From the EPR intensity point of view, the defect structures observed in CoMoO₄ have been masked by the significant domination of the defects in the NiMo/CoMoO₄ hybrid system having a very broad Gaussian EPR peak with the g -factor of $g = 2.3193$. The dipolar broadening is indeed arising from the spin-spin exchange interactions between Mo and Co paramagnetic

species and accordingly formed oxygen vacancies in a heterostructured hybrid system. As a result, the heterostructure formation can be further confirmed by the oxygen bridging between Ni/Mo–O–Co.

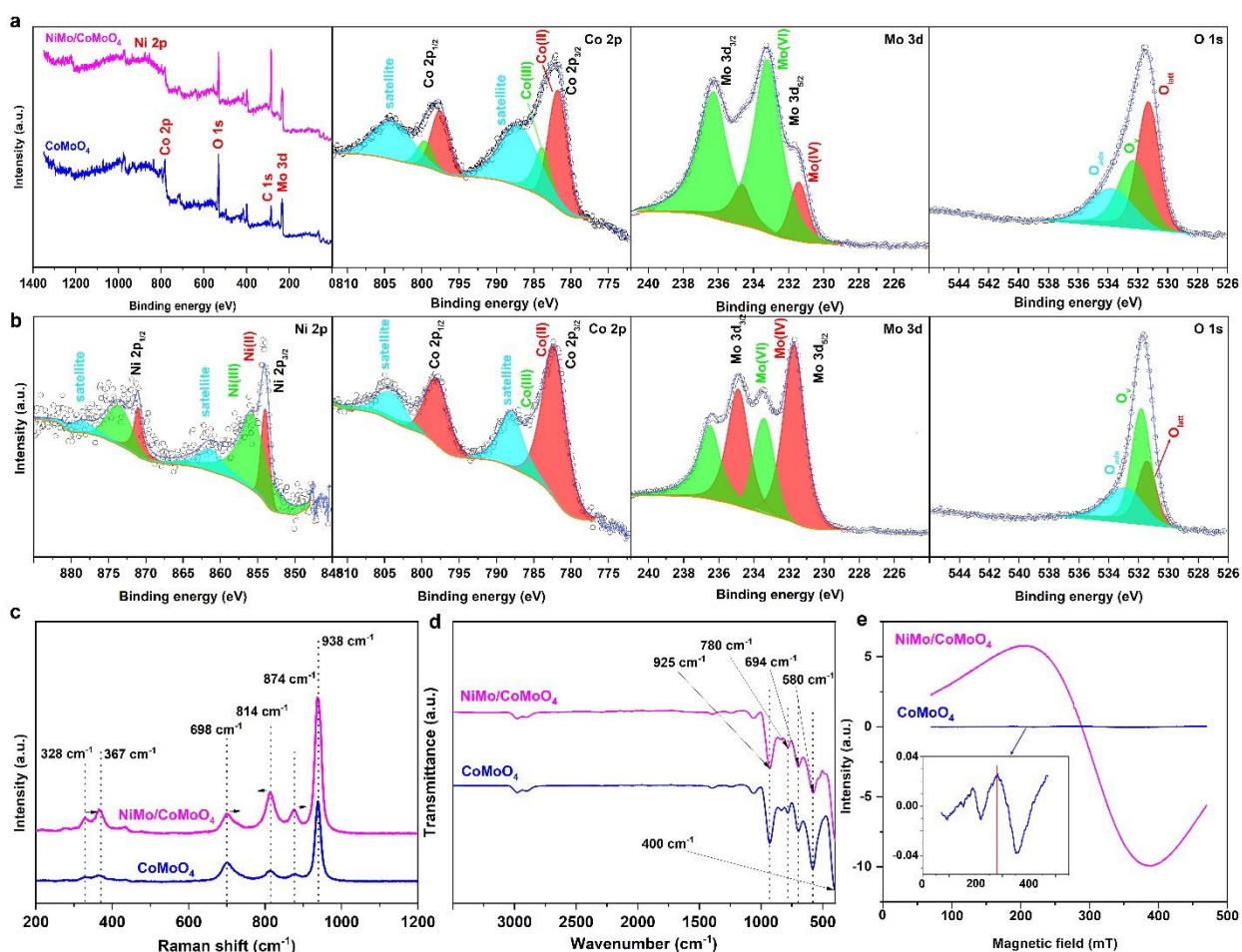


Figure 6. 3. Spectroscopic characterizations of the samples. a) From left to right XPS survey of CoMoO₄ and NiMo/CoMoO₄, XPS Co 2p, Mo 3d, and O 1s for CoMoO₄, b) From left to right, XPS Ni 2p, Co 2p, Mo 3d, and O 1s for NiMo/CoMoO₄, c) Raman spectra, d) FT-IR spectra, and e) X-band EPR spectra.

6.3.2. Electrochemical Studies

To assess the electrocatalytic ability of the electrodes for the alkaline HER a typical three-electrode configuration was employed. The HER polarization curves for each sample were obtained through LSV within the reduction potential window. Figure 6. 4a illustrates the electrocatalytic HER performances of the samples which includes 20 wt% Pt/C and bare NF for comparison. Moreover, the 3D bar graph in Figure 6. 4b presents the overpotential values at 10 and 50 mA cm⁻² current densities. From this figure, bare NF shows negligible HER behavior (385 and 630 mV @ 10 and 50 mA cm⁻²) while Pt/C

has superior activity (83 and 244 mV @ 10 and 50 mA cm⁻²). Among the prepared materials, NiMo/CoMoO₄ hybrid displayed the highest HER performance with low overpotentials of 102 and 357 mV at 10 and 50 mA cm⁻² followed by NiMo (244 and 417 mV @ 10 and 50 mA cm⁻²) and pristine CoMoO₄ (273 and 441 mV @ 10 and 50 mA cm⁻²). The tabulated data in Table D1 from the recent reports on similar works containing NiMo indicates that the HER performance of the hybrid catalyst in our study can be compared with these catalysts.

The HER kinetics of the catalysts were further examined via the Tafel plots by replotting the polarization curves which can be seen in Figure 6. 4c. As mentioned in the introduction section, hydrogen evolution in alkaline solutions is governed by two steps of Volmer. $\text{H}_2\text{O} + \text{e}^- + * \rightarrow \text{H}^* + \text{OH}^-$ (R3); i.e., water dissociation and adsorption of hydrogen at the catalyst, followed by Heyrovsky: $\text{H}^* + \text{H}_2\text{O} + \text{e}^- \rightarrow * + \text{OH}^- + \text{H}_2$ (R4) or Tafel: $2\text{H}^* \rightarrow \text{H}_2$ (R5); i.e., molecular hydrogen desorption by the combination of H^* . [18] According to previous studies, the higher Tafel slope ($> 120 \text{ mV dec}^{-1}$) suggests the Volmer step as the rate-determining step whereas the lower Tafel slope (30 or 40 mV dec⁻¹) implies the Tafel or Heyrovsky step as the rate-determining step. [253] Based on the Tafel slopes calculated from the polarization curves all the catalysts have similar results, running from 113 mV dec⁻¹ for Pt/C to $\sim 350 \text{ mV dec}^{-1}$ for NiMo/CoMoO₄ hybrid. This means that the reaction kinetics is governed by the adsorption and dissociation of water at the catalyst surface. [253] However, the presentation of reaction kinetics via LSV curves becomes a challenge while dealing with highly capacitive materials such as CoMoO₄. [8]

Several factors, such as applied potential, the presence of adsorbates, and mass transport in porous structures, can significantly influence the Tafel slope. It is important to emphasize that experimental observations have shown the Pt electrode, serving as the reference material for the HER, follows a Tafel path with a slope of 30 mV dec⁻¹. [220] However, as the applied potential increases, the catalyst surface becomes saturated with adsorbed hydrogen atoms, leading to accelerated atom-atom recombination. Consequently, the rate-limiting step shifts to a Volmer path, characterized by a Tafel slope of 120 mV dec⁻¹. In our work, the Pt/C electrode showed a Tafel slope of 113 mV dec⁻¹, verifying its validity with literature in alkaline conditions and approving its rate-limiting step, Volmer. In the case of the NiMo/CoMoO₄ electrode, the saturated surface covered with adsorbed intermediates brought about the same complication in terms of the Tafel

slope, resulting in a higher Tafel value compared to other as-fabricated electrodes. Additionally, non-faradaic/capacitive currents, iR drops, and conductivity of the catalysts often further complicate the derivation of Tafel slope via LSV.[254] It is worth noting that materials with higher double-layer capacitance contribute more to non-faradaic reactions, in which there is no chemical reaction for the charge transfer at the electrode/electrolyte interface.

To address this issue, Vrubel et al.[255] proposed a new approach to acquire a more reliable Tafel slope for a catalyst through EIS measurements within a certain potential window. In this approach, the Nyquist plots of the catalyst at various overpotentials at regular intervals are obtained, and the slope of overpotentials vs $\log(1/R_{ct})$ (where R_{ct} is the charge transfer resistance) gives the relevant precise Tafel slope. The Tafel slope received via this method is accurate as it depends only on the charge transfer capacity of the catalyst and excludes the effect of uncompensated resistance—the resistance exerted by the electrochemical interfaces.[8] Inspired by this study, we determined the Tafel slopes for three materials, namely, NiMo, CoMoO₄, and NiMo/CoMoO₄. For this, the EIS experiments were performed over the reduction potential from 100 mV to 200 mV vs RHE with a regular interval of 10 mV (view Figure D7).

The results showed completely different values compared to the Tafel values derived from LSV voltammograms. From Figure 6. 4f, the Tafel slope values demonstrated the following trend NiMo/CoMoO₄ (92 mV dec⁻¹) < CoMoO₄ (99 mV dec⁻¹) < NiMo (108 mV dec⁻¹). From more accurate results, we can claim that the hydrogen evolution mechanism on the as-prepared materials proceeds via Volmer–Heyrovsky (120–40 mV dec⁻¹).[256] More importantly, the EIS data recorded at 0.0 V vs RHE exhibited that NiMo possesses the minimum charge transfer resistance ($R_{ct} = 244.8 \Omega$), followed by NiMo/CoMoO₄ ($R_{ct} = 301.5 \Omega$) and CoMoO₄ ($R_{ct} = 463 \Omega$). All fitted data based on the equivalent circuit was tabulated for each sample and can be found in Tables D2–D4. In the representative equivalent circuit (Figure 6. 4e), R_s , R_p , and R_{ct} , respectively refer to resistance in solution, resistance from the porosity of the NF substrate, and charge transfer resistance. In addition, to fulfill the non-ideal behavior of the capacitive elements a constant phase element (CPE) was applied. Similarly, the double-layer capacitance in the interface of electrode/solution was taken into account through C_{dl} . It should be emphasized that the much larger C_{dl} value of NiMo/CoMoO₄ relative to those of NiMo

and CoMoO₄ accounts for its higher non-faradaic/capacitive behavior and in turn higher conventional Tafel slope through LSV curves.

To analyze the origin of the electrocatalytic activity of the as-fabricated electrodes—directly grown on NF, their ECSA values were determined through C_{dl} [257] at varying scan rates of 0.02 V s⁻¹ to 0.12 V s⁻¹ (Figure D8). As shown in Figure 6. 4d, the C_{dl} value of NiMo/CoMoO₄ has increased almost three-fold relative to pristine CoMoO₄ (2.71 mF cm⁻² vs 1.14 mF cm⁻²). Meanwhile, for NiMo NPs, the C_{dl} was obtained to be 1.3 mF cm⁻². The higher the C_{dl} , the more exposed active sites on the surface. With this in mind, the NiMo/CoMoO₄ with a higher C_{dl} value offers a large number of active sites. This is well in line with BET surface area results. The BET surface area for pristine CoMoO₄ and NiMo/CoMoO₄ were found to be 7.75 and 22.22 m²/g, respectively, which exhibits an almost three-fold increase in surface area in hybrid catalyst compared with CoMoO₄. The larger surface area ensures the accessibility of more active sites to promote the adsorption of reactants, accommodates the fast charge transfer, encourages the diffusion of electrolyte ions, and thereby elevates the electrocatalytic performance.[52, 232] The N₂ adsorption-desorption isotherms can be found in Figure D9. Further details derived from BET analysis were tabulated in Table D5. More importantly, the TOF, which defines the number of molecules reacted at each available catalytic site per unit time[258] was calculated for the as-fabricated electrodes. In this context, TOF was calculated via the following relation, $TOF = \frac{j \times A}{(2 \times F \times \frac{m}{M})}$ where j stands for current density at a specified overpotential (mA cm⁻²), A is the surface area of the working electrode (cm²), F represents the Faraday constant (96485 C mol⁻¹), m denotes the mass loading of the catalyst (g), and M indicates the molecular weight of the catalyst (g mol⁻¹).[259] In general the TOF measured within the overpotential range of 100–500 mV for hybrid catalyst was much large than that of CoMoO₄. For instance, at a low overpotential of 100 mV the TOF of NiMo/CoMoO₄ was obtained 0.012 s⁻¹ which is 6 times higher than that of CoMoO₄, 0.002 s⁻¹. Similarly, at a high overpotential of 500 mV, the TOF of NiMo/CoMoO₄ is 0.12 s⁻¹ compared to that of CoMoO₄, 0.077 s⁻¹ (refer to Figure 6. 4g). Finally, the NiMo electrode demonstrated identical TOF values to CoMoO₄ within the investigating potential range.

For practical applications of electrocatalysts, long-term durability in the alkaline condition is of high significance. The durability of NiMo/CoMoO₄ in 1.0 M KOH was explored at the fixed current density of 30 mA cm⁻² for 30 h through the

chronopotentiometry test. It must be borne in mind that the actual overpotential detected at 30 mA cm⁻² through the LSV curve is about 283 mV. As shown in Figure 6. 4h, the NiMo/CoMoO₄ catalyst exhibits an unsteady-state current during the initial four hours before reaching a steady-state current, after which it remains quite stable at around 300 mV for the next 26 h. This robust durability could be attributed to the exfoliation of the nanostructures while the gases are formed and released, bringing about the sufficient active surface area on the electrode. The inset picture in Figure 6. 4h depicts the LSV curves before and after 30 h of long-term HER durability. The overpotential at 10 mA cm⁻² increases from 102 mV to 163 mV, confirming its competence after 30 h being exposed to 30 mA cm⁻² reduction current. To investigate the possibility of dissolution and redeposition of Pt spring—the counter electrode—on the electrode material, we carried out the ICP-MS characterization on the electrolyte solution following long-term HER stability. The results showed that the concentration of Pt inside the solution is infinitesimally low, 0.037 ppb, confirming that it cannot affect the electrocatalysis results. Therefore, the possibility of Pt dissolution and redeposition on the working electrode in this study can be safely ruled out.

6.3.3. *Post- Electrocatalysis Characterization*

To examine the changes after the long-term alkaline HER stability test, we carried out further analyses on the NiMo/CoMoO₄ electrode. The SEM image shown in Figure 6. 5a indicates a dramatic change in the topography and morphology of the samples compared to the fresh sample (see Figure 6. 2c). Even though the nanoflowers and nanorods disappeared, the interwoven nanosheets which were the building blocks of the catalysts can be observed on the NF substrate. Additionally, the TEM photograph in Figure 6. 5b shows images of nanosheets and NPs, belonging to CoMoO₄ and NiMo NPs. The TEM images before and after long-term HER durability are dissimilar in terms of crystallinity, meaning that the degree of crystallinity is reduced after the durability test. However, the two green and red squares delineate two distinctive nanoparticles, one with an interplanar spacing of 0.217 nm, corresponding to NiMo NP, and the other with a d-spacing of 0.201 nm, consistent with Ni(111). With this finding, it can be concluded that: i) NiMo NPs are very stable under alkaline conditions even at high current densities like 30 mA cm⁻² and ii) Ni with higher oxidation states reduced to the metallic state during continuous hydrogen evolution.

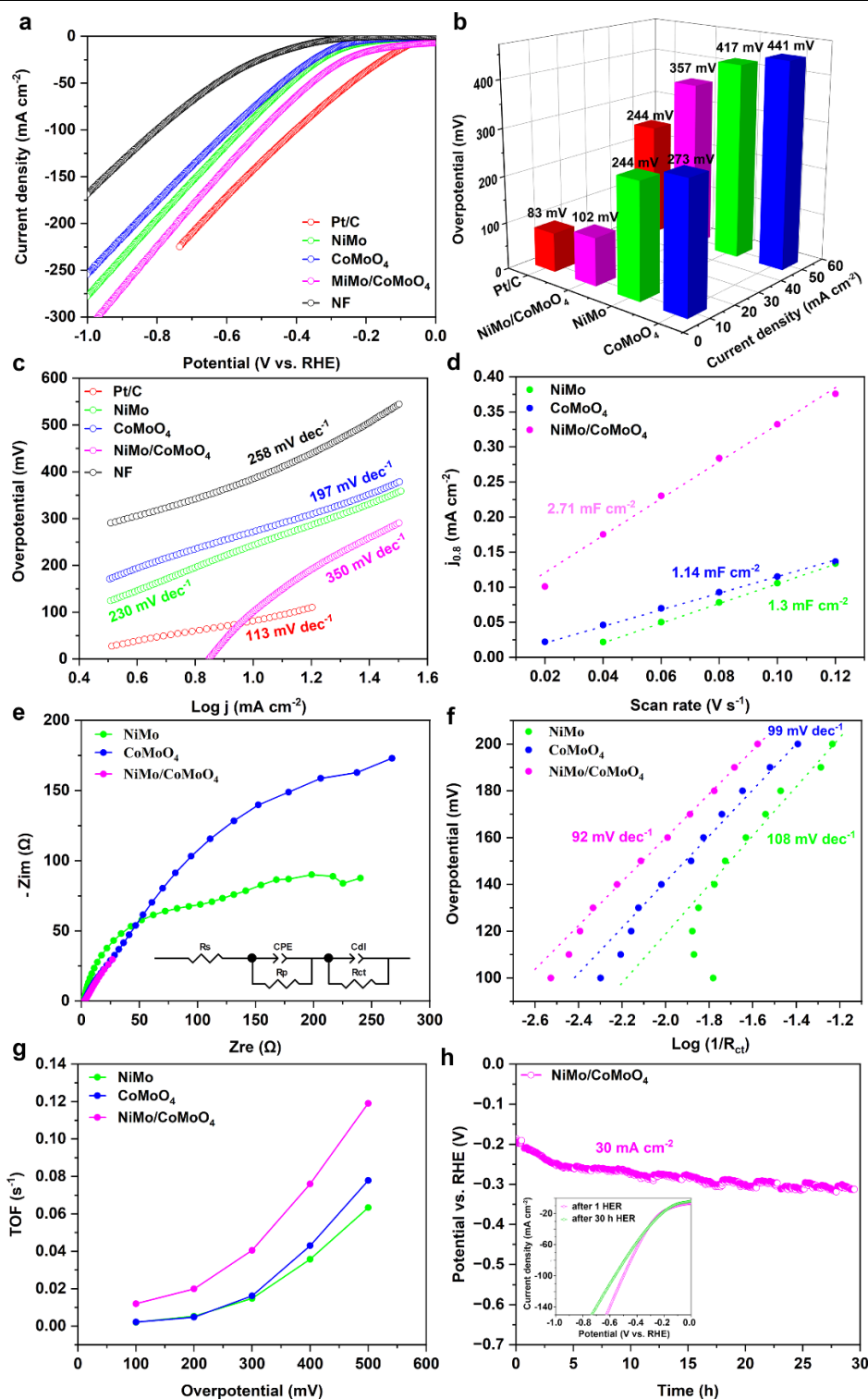


Figure 6. 4. Electrocatalytic hydrogen evolution performances in 1.0 M KOH. a) HER polarization curves of the samples, b) 3D bar graphs of overpotentials at 10 and 50 mA cm⁻², c) HER Tafel plots obtained by polarization curves, d) Capacitive current density versus scan rate curves for ECSA measurements, e) EIS spectra recorded at 0 V versus RHE, f) HER Tafel plots derived from EIS experiments, g) TOF (s⁻¹) versus overpotential (mV), and h) Long-term HER durability test of NiMo/CoMoO₄ at an applied current density of 30 mA cm⁻² (inset: HER polarization curves of NiMo/CoMoO₄ before and after long-term HER).

To identify the oxidation states on the surface, post-stability XPS results (Figure 6. 5c) were analyzed. Ni 2p core-level spectrum exhibited two doublet peaks with corresponding satellites. The peaks around BEs of 848.5–850 eV, 855.0–855.4 eV, and 860.5–861.2 eV can be assigned to Ni⁰, Ni(II), and the Ni shake-up satellite, respectively.[260] The Ni 2p XPS corroborated the results found with HR-TEM, the reduction in oxidation states of Ni after long-run HER is pronounced. Meanwhile, the atomic proportion of Ni slightly mounted up relative to the fresh sample (0.89% → 0.92%), attributing to the emergence of metallic Ni. Interestingly, the Co 2p XPS spectrum demonstrated both Co(II) and Co(III) states. Moreover, the atomic proportion of both oxidation states of Co increases from 3.06% to 3.60% for Co(II) and from 0.15% to 4.77% for Co(III), implying the higher electron density of Co sites after the HER durability test. The meaningful increase in the electron density of Co might be a result of the preference for the adsorption of OH species after the dissociation of water molecules. Furthermore, the signals that appeared at BEs of 779.75 and 780.93 eV revealed the XPS peak shift in Co to lower BEs compared to the fresh hybrid sample (refer to Figure 6. 3b, Co 2p XPS spectra). In the case of the Mo 3d XPS spectrum, the fitted data showed the presence of only one oxidation state at the BE of 231.91 eV which can be ascribed to Mo(IV) with a slight shift to a higher BE value. Further, the atomic proportion of Mo 3d drastically declined to 0.16% compared to the fresh sample (6.01%). The dramatic decline in the atomic proportion of Mo 3d can likely be due to the complete reduction of Mo(VI) during long-term hydrogen evolution. Finally, the O 1s deconvoluted spectrum exhibited three peaks similar to the fresh sample. However, the atomic proportion of all three peaks elevated after 30 h HER durability measurement. Based on these observations, it is evident that Ni and Mo are ideal locations for H⁺ adsorption and subsequent evolution to molecular H₂, as both metals donate electrons. As a result, localized positive charges appear on the metal surfaces, to neutralize the positive charges, Ni and Mo attract electrons from the surrounding electrolyte and are reduced to lower oxidation states. Conversely, Co atoms in proximity to oxygen vacancies are the preferred site for OH⁻ adsorption.

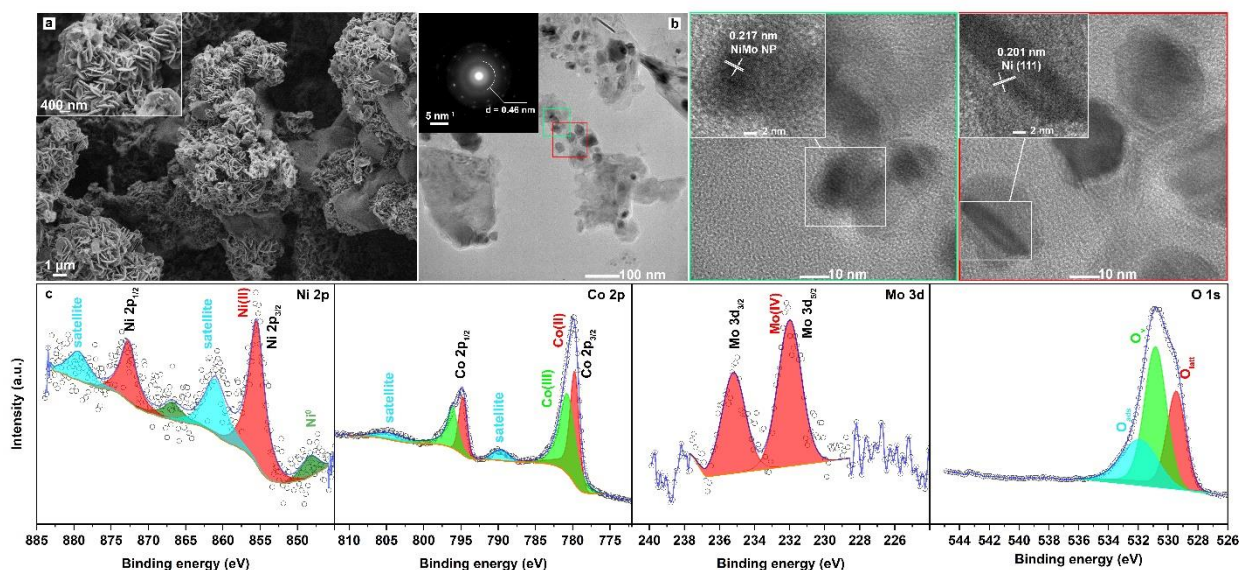


Figure 6. 5. Post-electrolysis characterizations of NiMo/CoMoO₄ after long-term HER test. a) SEM image (inset: high magnification SEM image), b) TEM and HR-TEM images (inset: SAED pattern), and c) XPS Ni 2p, Co 2p, Mo 3d, and O 1s spectra.

6.4. Proposed Mechanism

Based on the findings, herein we propose a possible mechanism that can take place during hydrogen evolution electrocatalysis. According to the XPS, HR-TEM, and EPR outcomes, once NiMo and CoMoO₄ are combined, a heterostructure can be formed via Ni/Mo–O–Co. To elucidate this point, we must explain that i) XPS spectra for Ni 2p revealed a peak shift after coupling two components in favor of higher electron density, ii) HR-TEM results exhibited oxygen defects in both CoMoO₄ and hybrid samples, and iii) EPR characterizations demonstrated a huge peak for hybrid catalyst due to the presence of Ni/Mo–O. Furthermore, EPR analysis confirmed the presence of oxygen defects within the CoMoO₄. Therefore, the oxygen vacancy-confined NiMo/CoMoO₄ heterostructure was successfully created on NF. The hydrogen evolution in the alkaline solution might occur as follows: once the H₂O molecules dissociate into H and OH (refer to R3), metallic NiMo would act as a good proton acceptor, at the same time, the heterostructure with oxygen vacancy modification can be a good adsorber for OH species.

This means the metallic side has a preference for the adsorption of H, whereas the oxygen vacancy-confined side has a preference for the adsorption of OH. In the subsequent step, with the oxygen bridging formation between Ni/Mo–O–Co,[232, 242–244] and in turn higher electron density on Ni sites—higher electronegativity relative to Co—as a result of electron localization around Ni, the recombination of adsorbed H* to

H₂ can take place (refer to R5) and be accelerated compared with the individual components of NiMo and pristine CoMoO₄ (view schematic illustration of HER mechanism in Figure 6. 6a). To complement this observation, Kai Ling Zhou et al.[52] performed a similar study to investigate the reaction barrier on the Pt single-atom catalyst coupled with Ni/NiO heterostructure. Based on this work, the kinetics of alkaline HER is mainly dependent on how OH and H bind to the active sites on the catalyst's surface. With the DFT calculations they proved that metallic Ni has a preference for the adsorption of H while NiO did not show satisfactory capacity for the adsorption of both OH and H. Conversely, oxygen vacancy-modified NiO displayed elevated ability for the adsorption and stabilization of OH species. With this, the oxygen vacancy in the interface of Ni/NiO can minimize the energy barrier for the splitting of the water molecule into OH and H. Based on their findings, Pt coupled-Ni/NiO heterostructure demonstrated the strongest H₂O adsorption ability and largest energy release of -0.09 eV for water dissociation in Volmer step compared with Pt coupled-Ni (0.08 eV) and Pt coupled-NiO (1.01 eV). Eventually, they obtained the optimal value for ΔG_{H^*} for Pt coupled-Ni/NiO hybrid (-0.07 eV) to improve HER relative to Pt coupled-Ni (-0.38 eV) and Pt coupled-NiO (0.74 eV).

Finally, the quantity of hydrogen evolution on the NiMo/CoMoO₄ was carried out via gas chromatography through chronopotentiometry at 10 and 100 mA cm⁻² for 150 min each, presented in Figure 6. 6b. The Faradaic efficiency was estimated using $FE = \frac{n_{exp}}{Q/ZF}$, where, n_{exp} stands for the number of moles of H₂ experimentally produced at 10 or 100 mA cm⁻², Q (C) refers to the total amount of charge, Z is the number of transferred electrons (i.e., in HER, $Z = 2$), and F is the Faraday's constant (96485 C mol⁻¹).[52, 261] The results can be visualized in Figure 6. 6c. The Faradaic efficiency for H₂ production using the hybrid catalyst was determined to be 100% at 10 mA cm⁻² and 86–95% at 100 mA cm⁻², confirming its high efficiency in generating hydrogen.

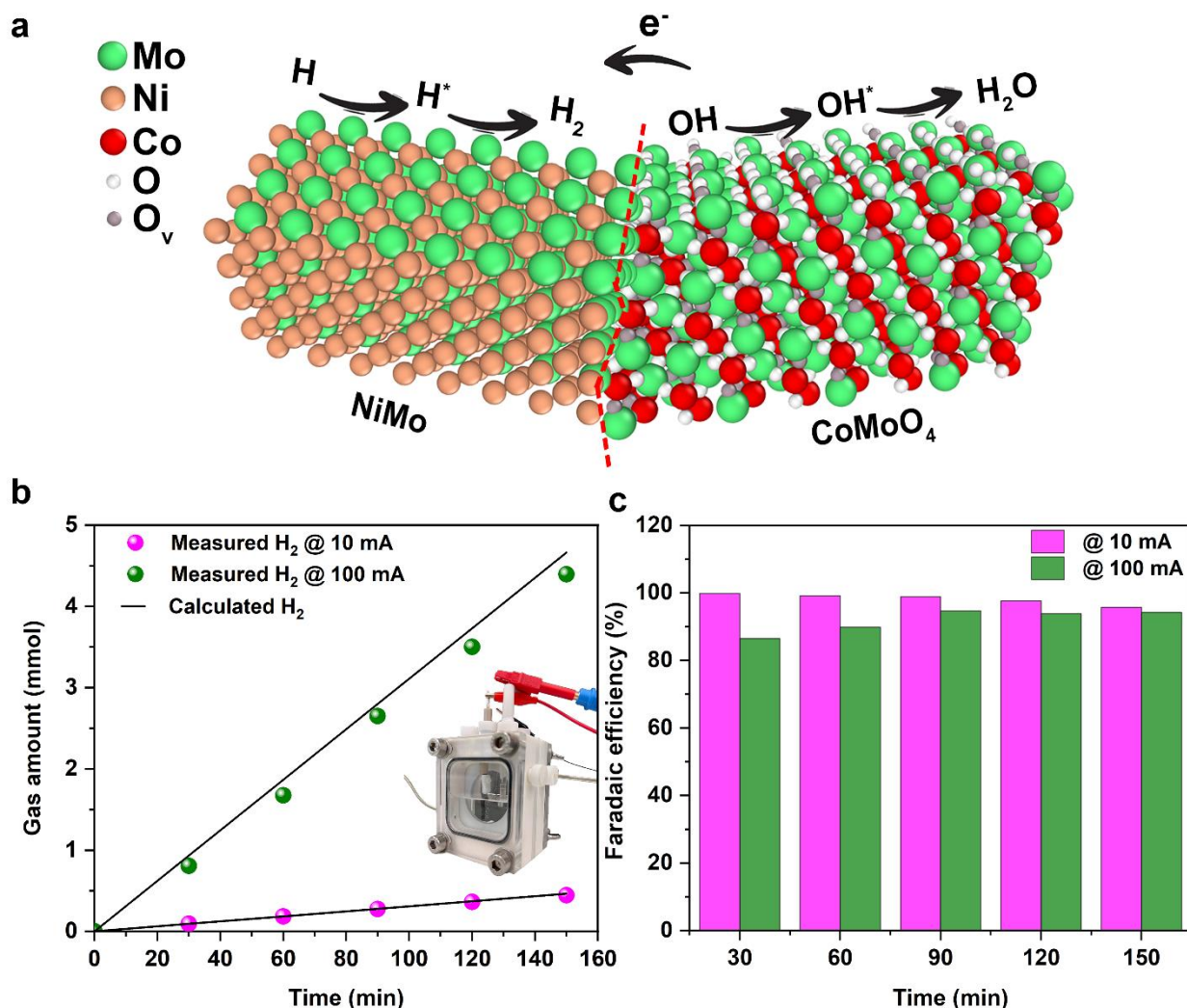


Figure 6. a) Schematic presentation of proposed HER mechanism, b) Amount of gas theoretically calculated and experimentally measured for HER using NiMo/CoMoO₄ at 10 mA cm⁻² (inset: homemade electrolysis cell for electrochemical measurements), and c) Quantification of Faradaic efficiency derived from calculated and measured H₂.

6.5.CONCLUSIONS

In summary, we proved a competent and stable hydrogen evolution catalyst can be designed by marrying inexpensive components of metallic NiMo and oxygen vacancy-confined CoMoO₄ on the NF. The heterostructure formed between two components brought about an electron transfer from CoMoO₄ to the NiMo side, resulting in higher electron density on the metallic side. Therefore, following water dissociation into H and OH, the metafile NiMo could preferably adsorb H whereas oxygen vacancy-modified CoMoO₄ might show affinity toward OH species. The electrochemical active surface area for the NiMo/CoMoO₄ hybrid grew almost three-fold compared to pristine CoMoO₄.

Moreover, the BET surface area exhibited similar behavior, indicating a three-fold enlargement of surface area in NiMo/CoMoO₄ relative to CoMoO₄. The NiMo/CoMoO₄ reached 10 mA cm⁻² at a low overpotential of 102 mV for the alkaline HER, approaching Pt/C performance (83 mV). The HER mechanism was studied via EIS experiments within the reduction window of 100–200 mV, the hybrid catalyst demonstrated the smallest Tafel slope of 92 mV dec⁻¹, implying the hydrogen adsorption (H*) via Volmer and its subsequent desorption (H₂) through Heyrovsky. The Faradaic efficiency for the H₂ production on the fabricated hybrid catalyst confirmed the efficiency as 100% at 10 mA cm⁻² and 86–95% at 100 mA cm⁻². This study presents an affordable, durable, and high-performance catalyst for the alkaline hydrogen evolution which can rival the noble-metal-based catalyst.

CHAPTER 7

IN-Situ DESIGN OF A NANOSTRUCTURED INTERFACE BETWEEN NiMo AND CuO DERIVED FROM METAL–ORGANIC FRAMEWORK FOR ENHANCED HYDROGEN EVOLUTION IN ALKALINE SOLUTIONS

7.1.Introduction

Organic–inorganic hybrid materials including metal–organic frameworks (MOFs) and zeolitic imidazolate frameworks (ZIFs), offer promising features due to their adjustable porosity and structure. Among these, MOF-derived materials, characterized by a controllable surface area and functional groups, are highly potential for electrocatalytic applications.[262, 263] Notably, Cu-BDC MOF (CCDC no. 687690), a well-known MOF, is synthesized from copper nitrate and the widely available, environmentally safe terephthalic acid (BDC).[264, 265] Cu-BDC demonstrates compelling traits, such as strong stability in aqueous environments within diverse pH ranges, attributed to the robust coordination interaction between copper cations and the –COOH group of BDC.[264] In some reports, however, it is claimed that the direct usage of MOFs as catalysts is not desirable due to their poor conductivity, limited accessibility of active metallic sites, and low stability in aqueous environments.[266, 267] Consequently, numerous endeavors have been undertaken to augment the electrical conductivity of materials based on MOFs through methods such as heat treatment at high temperature [265, 268] or combining them with conductive supports.[267, 269]

According to the literature, the MOF-derived transition metal oxide (TMO) catalysts tend to undergo self-aggregation, resulting in the loss of exposed active sites and a concomitant reduction in mass transfer during electrocatalysis.[270, 271] Hence, there is a keen anticipation and a challenging task of exploring alternative approaches or carefully selecting suitable MOF precursors to fabricate novel electrocatalysts based on TMOs with improved performance for the HER.[270] In recent reports, it has been revealed that enhancing the performance of Cu-based materials for the HER is achievable through the meticulous design of their compositions, structures, and morphologies.[272, 273] One of these strategies that stands out among others could be the heat treatment of Cu-MOF with which the carbon-decorated copper oxide is attainable with flexible structure and tunable porosity at molecular level.[274, 275] Carbon-decorated TMOs, derived from MOFs, emerge as promising candidates for the HER, attributed to their enhanced electrocatalytic stability even under harsh reaction conditions.[276, 277]

In the pursuit of high-performance electrode materials, in addition to the above-mentioned approach, significant endeavors have been dedicated to the strategic design of electrode materials, featuring precisely defined micro/nanostructures through the fabrication of composites and hybrid materials.[231] Recently, we reported a

heterostructured HER electrocatalyst consisting of oxygen vacancy-confined CoMoO₄ and NiMo alloy that showcased its high activity and durability under alkaline electrolyte.[278] It is believed that incorporating Ni with other metals allows for the fine-tuning of the electronic structure, consequently enhancing catalytic activity, examples being NiFe, NiCo, and NiMo alloys.[54, 279, 280] Particularly, NiMo alloy is well-established as a highly effective electrocatalyst for the HER in alkaline electrolytes.[54, 281] Hence, through the deliberate design of heterointerfaces, it becomes feasible to effectively adjust electron distribution, generate numerous active sites, and amplify the chemical adsorption capability of the catalyst. This, in turn, leads to a significant enhancement in electrochemical activity. Additionally, elevating the number of exposed active sites can further augment the electrocatalytic activity.[282, 283] However, the exploration and documentation of hybrid systems derived from Cu-MOFs have been scarce and limited.

In this study, we introduce a novel electrocatalyst, Cu-BDC MOF-derived NiMo/CuO, for alkaline HER. The fabrication process involved a hydrothermal procedure to grow the materials directly on a Cu-coated NF substrate, followed by a heat treatment step to produce the final composite on the NF skeleton. The distinctive interface between the two components significantly enhanced electron transfer during the reduction process. As a result, this catalyst demonstrated outstanding performance, achieving 10 mA cm⁻² at a low overpotential of 85 mV.

7.2.Experimental Section

7.2.1. Catalyst Preparation

7.2.1.1.Materials

1,4-benzenedicarboxylic acid [terephthalic acid/1,4-BDC, Sigma-Aldrich, 98%], *N,N*-dimethylformamide [DMF, Sigma-Aldrich], Polyvinylpyrrolidone (PVP, Sigma-Aldrich), nickel chloride hexahydrate (NiCl₂·6H₂O, Sigma-Aldrich, 99.9% trace metals basis), sodium molybdate dihydrate (Na₂MoO₄·2H₂O, Sigma-Aldrich, ACS reagent, ≥99%), sodium borohydride (NaBH₄, Sigma-Aldrich), copper(II) sulfate pentahydrate (CuSO₄·5H₂O, ACS reagent, ≥98.0%), and copper(II) nitrate trihydrate (Cu(NO₃)₂·3H₂O, Sigma-Aldrich, puriss. p.a., 99-104%) were purchased and used without any prior treatment.

7.1.1.1.Synthesis of NiMo nanoparticles

We discussed the preparation protocol of NiMo nanoparticles (NPs) in our recent publication.[278] Briefly, the synthesis of NiMo NPs involved dissolving 1g of PVP in 50 mL of deionized (DI) water, adding Ni and Mo precursors ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$), followed by the addition of NaBH_4 . After rigorous stirring, the resulting black suspension was washed, dried, and heated under air atmosphere at 500 °C for 2 h to obtain crystalline NiMo NPs.

7.2.1.2.Synthesis of NiMo/Cu-BDC MOF and NiMo/CuO Derived from Cu-BDC MOF on NF

The commercial NF (1.5 cm × 3 cm) underwent a series of treatments to remove contaminants from its surface, including ultrasonication with 2.0 M HCl solution, acetone, DI water, and ethanol, each for 10 minutes. Subsequently, the NF was dried by exposing it to the open air to ensure the removal of oxides and other impurities. To grow Cu-BDC on the NF, the first step involved electrodeposition of Cu on the NF using a 0.05 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution. A three-electrode cell configuration was employed, with a piece of Cu foil as the counter electrode and the Calomel electrode as the reference electrode. The pre-treated NF, which was previously subjected to heat treatment under ambient environment at 550 °C for 2 h, served as the working electrode. The electrodeposition process was carried out via a chronopotentiometry experiment with a current of -0.02 A applied for 2 ½ h. The optical microscope image of Cu-coated NF under polarized light can be seen in Figure E1.

For the fabrication of NiMo/Cu-BDC on the Cu-deposited NF, a solution was prepared by dissolving 2 mmol $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 2 mmol terephthalic acid separately in 20 ml DMF. The two solutions were mixed and stirred for 30 min, resulting in a blue solution. Subsequently, a quantified amount of NiMo (10 wt %) was added to the mixture and stirred for another 30 min, creating a black solution. To ensure thorough dissolution and mixing, the black solution was ultrasonicated for an additional 30 min. The prepared mixture was then poured into a 50 mL Teflon-lined stainless-steel autoclave, where the previously Cu-deposited NF was added. The autoclave was tightly sealed and placed in an oven, maintained at 120 °C for 24 h. After cooling down to room temperature naturally, the product was rinsed with DI water and ethanol before being vacuum dried overnight at 80 °C. The final product was annealed at 500 °C for 2 h in air. The schematic illustration in Figure 7. 1 briefly describes the synthesis process. The pristine Cu-BDC was prepared

In-situ Design of a Nanostructured Interface between NiMo and CuO Derived from Metal–Organic Framework for Enhanced Hydrogen Evolution in Alkaline Solutions 149 following the identical steps without addition of NiMo to the solution. In this article, for ease of reference, we assign the labels Cu-BDC_{Cal.} and NiMo/Cu-BDC_{Cal.} to the Cu-BDC and NiMo/Cu-BDC samples after undergoing heat treatment, respectively.

7.2.1.3. Preparation of Pt/C on NF

1 mg of commercial 20 wt % Pt/C was ultrasonically dispersed in a 300 μL ethanol and 200 μL DI water solution for 30 min. Subsequently, 10 μL of Nafion solution was added and sonicated for an additional 30 min to create a homogeneous ink. This ink was then pipetted onto a NF substrate, achieving a mass loading of about 1 mg cm⁻².

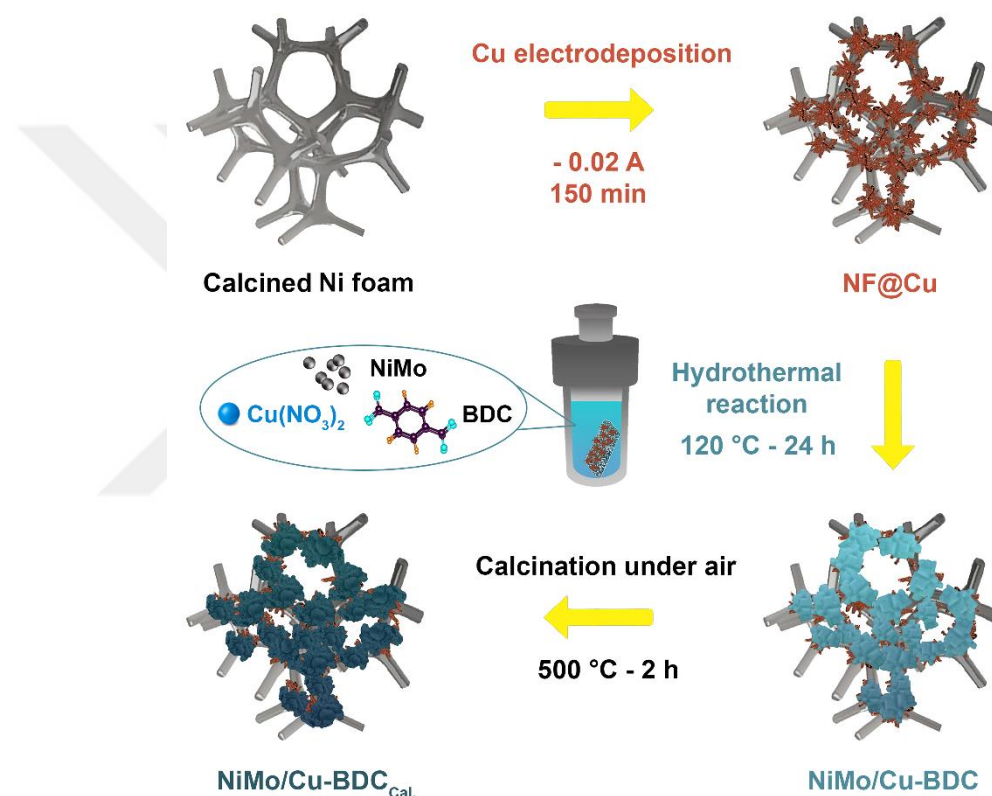


Figure 7. 1. Schematic illustration of preparation procedure of NiMo/Cu-BDC_{Cal.} (CuO derived from Cu-BDC MOF) on NF.

The crystal phase and purity of the synthesized materials were assessed using XRD analysis performed with a Rigaku Mini Flex 600 instrument equipped with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The morphology was characterized via field emission-scanning electron microscopy (FE-SEM; Zeiss Ultra Plus), coupled with an EDS detector, Bruker Xflash 5010 offering a spectral resolution of 123 eV. For a comprehensive microstructural analysis, including SAED, examination of lattice fringes, HAADF-STEM images and corresponding EDS-STEM mappings, (HR-TEM; Hitachi HF5000 200 kV

(S)TEM) was employed. The surface composition and oxidation states were probed using (XPS, Thermo Scientific K-Alpha) with an Al K α monochromator source emitting at 1486.6 eV. The XPS spectra were appropriately calibrated with respect to the binding energy (BE) of C 1s, set at 284.50 eV. The vibrational modes of the molecules were investigated through Raman spectroscopy employing a Raman microscope (RENISHAW INVIA) with a 532 nm excitation laser source. Identification of functional groups was accomplished using Fourier transform-infrared spectroscopy (FT-IR, JASCO 6800 full vacuum & FT-IR microscope). The Brunauer-Emmett-Teller (BET) specific surface area was ascertained through N₂ adsorption-desorption isotherms, utilizing a Micromeritics ASAP 2010 instrument.

7.2.2. *Electrochemical Characteristics*

All electrochemical investigations were executed using an AutoLab Potentiostat Galvanostat (PGSTAT302N, fabricated in the Netherlands) within a conventional three-electrode setup immersed in an alkaline medium (1.0 M KOH). The reference electrode employed was a reversible hydrogen electrode (RHE; HydroFlex), while a platinum (Pt) spring was implemented as the counter electrode. Working electrodes were comprised of catalysts grown on nanostructured substrates (0.5 cm $\times$ 1 cm). Linear sweep voltammetry (LSV) profiles were recorded within the region of hydrogen evolution reaction (HER) potentials (ranging from 0 to -1 V) at a scanning rate of 5 mV s⁻¹. HER overpotentials were evaluated at current densities of 10 and 50 mA cm⁻². The acquired LSV data were subsequently transformed into Tafel plots. Electrochemical C_{dl}, pertinent to CV conducted at varying scan rates (0.02, 0.04, 0.06, 0.08, 0.1, 0.12, 0.14, 0.16, 0.18, and 0.2 V s⁻¹) across the potential window from 0.7 to 0.8 V vs RHE, was used to determine the ECSA. For assessing long-term HER stability, chronopotentiometry tests were performed at a consistent applied current density of 30 mA cm⁻² for a duration of 50 h. EIS measurements were conducted at -300 mV vs RHE, spanning a frequency spectrum from 100 kHz to 0.1 Hz. All electrochemical data were presented without considering iR correction, as the calculated iR drop was determined to be 11.7 Ω , which exhibited negligible influence on the outcomes.

7.3.RESULTS AND DISCUSSION

7.3.1. Structural Studies

The XRD technique was employed to investigate the crystalline composition of the as-obtained samples. Figure E2 illustrates the XRD patterns of NiMo NPs before and after heat treatment. Obviously, the single broad peak at 2θ around 45° for NiMo before heat treatment is an indicative of an amorphous structure. On the other hand, the XRD pattern of NiMo after heat treatment shows a distinct difference. Our analysis confirmed the transformation of NiMo to NiO (ICSD#9866) and MoO_2 (at $2\theta = 26^\circ$ and 37.2° marked by ♥) after applying heat treatment. The XRD results of Cu-BDC and NiMo/Cu-BDC scratched off from substrate were provided in Figure 7. 2a. It can be found that all the reflections are attributed to the simulated pattern from the single crystal data of the Cu-BDC (CCDC#687690). Finally, the diffraction peaks of $\text{Cu-BDC}_{\text{Cal.}}$ and $\text{NiMo/Cu-BDC}_{\text{Cal.}}$ can be visualized in Figure 7. 2b. According to these results both MOF-bearing samples transform to CuO (ICSD#67850) once the heat treatment is applied. There are no other forms of copper oxide in these samples, demonstrating the high purity of final products. The single minor peak (marked by ♦) appeared within the diffraction pattern of $\text{NiMo/Cu-BDC}_{\text{Cal.}}$, displays the presence of NiMo in the sample. It is noteworthy that the weak and broad peak at $2\theta = 26^\circ$ for both samples after calcination confirms the carbonization as a result of the heat treatment, corresponding to the (002) plane of the graphitized carbon.

Raman spectroscopy was used to monitor structural evolution during the thermal treatment process of NiMo, Cu-BDC, and NiMo/Cu-BDC. The Raman characteristic peaks for both Cu-BDC and NiMo/Cu-BDC were displayed in Figure E3a. The architecture of Cu-BDC exhibits a 3D network, interconnecting the two-dimensional (2D) layers comprising porous copper(II) dicarboxylate —so-called copper paddle wheels— by the DMF solvent (refer to Figure E4). In the higher frequency range ($\geq 900 \text{ cm}^{-1}$), the Raman bands predominantly arise from vibrational modes of the BDC linkers. Specifically, the band observed at 1620.7 cm^{-1} corresponds to the phenyl mode ($\text{C}=\text{C}$ stretching mode of BDC). Additionally, the feature at 1530.9 cm^{-1} can be attributed to the asymmetric in-plane vibration of COO, while the bands at 1436.3 and 1419 cm^{-1} are indicative of the symmetric vibration of COO. In the low frequency region ($100\text{--}750 \text{ cm}^{-1}$), Cu-BDC and NiMo/Cu-BDC before heat treatment exhibited a more complex

Raman spectra because of the presence of vibrational modes of metal (Cu) oxide clusters. Three bands at 456.8, 400, and 326 cm^{-1} are attributed to Cu–O species.[284] As shown in Figure E3b, a set of strong Raman peaks were observed for NiMo after heat treatment. The bands observed at 939.1, 893.7, and 820.3 cm^{-1} are ascribed to the Mo–O vibrations and in good agreement with previous reports.[285] The bands positioned at 367 and 341.4 cm^{-1} correspond to symmetric torsional vibrations of O–Mo–O.[278] Interestingly, the new weak peak appeared at 119.6 cm^{-1} and could be attributed to the lattice deformation mode for MoO_2 species.[285] Finally, the Raman spectroscopy for $\text{Cu-BDC}_{\text{Cal.}}$ and $\text{NiM/Cu-BDC}_{\text{Cal.}}$ demonstrated three signals at 280, 335, and 525 cm^{-1} (shown in Figure 7. 2c) corresponding to the A_g , $B_g^{(1)}$ and $B_g^{(2)}$ modes of the CuO single crystal, respectively.[286]

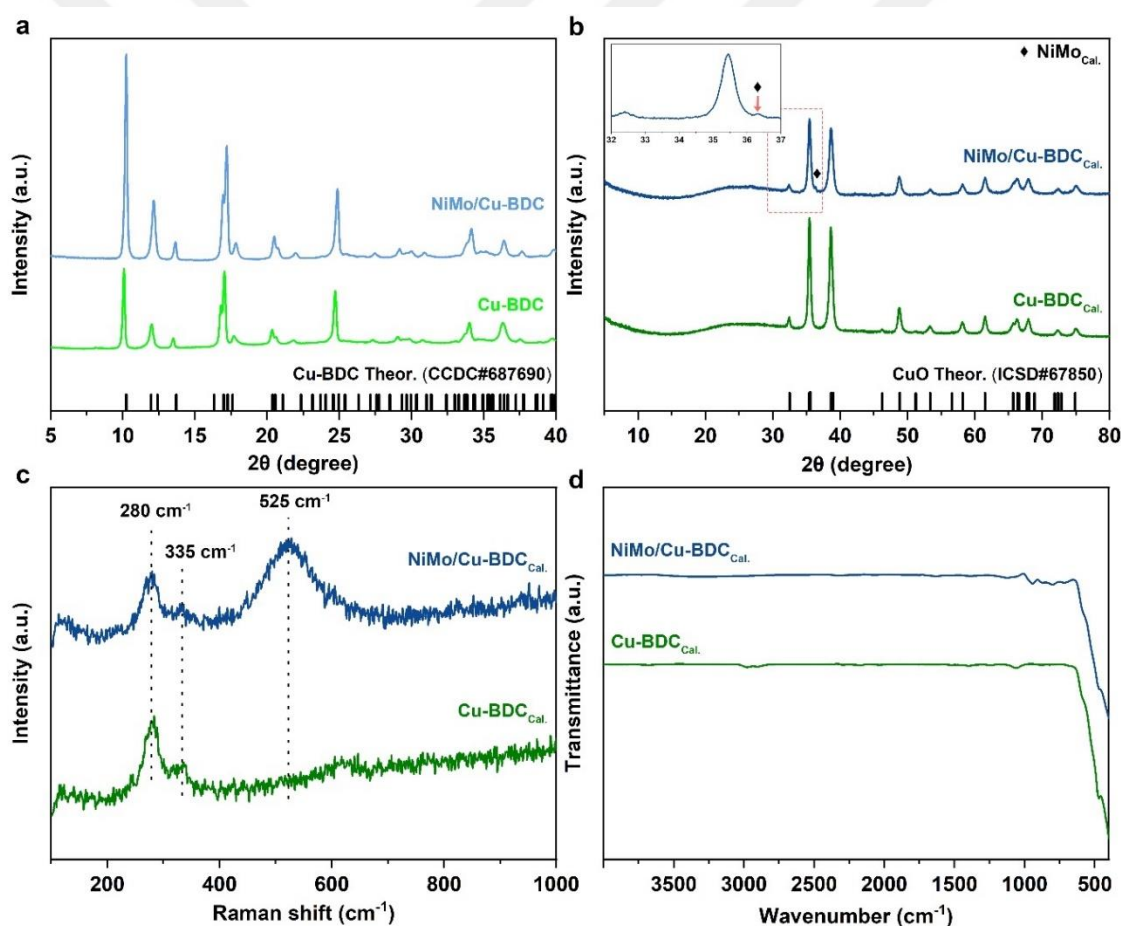


Figure 7. 2. Structural and spectroscopic characterizations. a) XRD patterns of Cu-BDC and NiMo/Cu-BDC stripped off from NF, b) XRD patterns of $\text{Cu-BDC}_{\text{Cal.}}$ and $\text{NiMo/Cu-BDC}_{\text{Cal.}}$ stripped off from NF, c) Raman spectra for $\text{Cu-BDC}_{\text{Cal.}}$ and $\text{NiMo/Cu-BDC}_{\text{Cal.}}$, and d) Ft-IR spectra for $\text{Cu-BDC}_{\text{Cal.}}$ and $\text{NiMo/Cu-BDC}_{\text{Cal.}}$.

Figure E5a represents the FT-IR spectra of prepared Cu-BDC and NiMo/Cu BDC composite. The two sharp characteristic bands at 1386 and 1608 cm^{-1} are indexed to the

symmetric and asymmetric stretching modes of --COOH respectively.[287, 288] The peaks at 829 and 887 cm^{-1} correspond to the out-of-plane and in-plane aromatic C–H bending.[289, 290] The bands at 755 and 1501 cm^{-1} are related to phenyl ring.[291, 292] The observed peaks at 458 and 567 cm^{-1} can be considered as the stretching vibration peaks of Cu–O.[288, 292] The small peak at about 2900 cm^{-1} is attributed to the aromatic C–H stretching vibration.[290] The band at 1666 cm^{-1} is assigned to the carbonyl group in DMF [293]. However, NiMo/Cu-BDC composite compared to pristine Cu-BDC exhibited a slight blueshift around $500\text{--}700\text{ cm}^{-1}$ which suggests that there might be some possible interactions between NiMo and Cu-BDC. Figure E5b illustrates the absorption bands for NiMo NPs before and after heat treatment. The bands located at $650\text{--}960\text{ cm}^{-1}$ were ascribed to the vibrations of Mo–O and Mo–O–Mo.[294–296] Moreover, the FT-IR peaks appeared at 1287 and 485 cm^{-1} were both due to the Ni–O bonds.[294, 297] After calcination, the FT-IR patterns of $\text{Cu-BDC}_{\text{Cal}}$ and $\text{NiMo/Cu-BDC}_{\text{Cal}}$ displayed a vibration peak around 470 cm^{-1} that can be related to Cu–O (Figure 7. 2d).

The morphological characteristics of the specimens were investigated utilizing the FE-SEM technique. The SEM depiction of NiMo before the process of calcination is presented in Figure E6, displaying the presence of highly agglomerated nanoscale particles with an approximate dimension of below 20 nm . The SEM micrographs portraying Cu-BDC and NiMo/Cu-BDC, cultivated on the NF backbone, are observable in Figure 7. 3a,b. These micrographs illustrate polyhedral structures with dimensions extending to a magnitude of several hundred nanometers. In contrast, the SEM images of Cu-BDC and NiMo/Cu-BDC post-thermal treatment exhibit marked disparities relative to their pre-thermal treatment SEM images. As demonstrated in Figure 7. 3c,d, both samples exhibit a spherical morphology typified by compact aggregation, attributed to the transition of the Cu-BDC MOF template into CuO@C . Figure E7 presents a better view on the morphology, topography, and uniform distribution of catalysts on the NF. The dimensions of these aggregated particulates are not readily ascertainable.

Further microstructural features were explored through the utilization of TEM and HR-TEM analyses. The TEM imagery portraying NiMo NPs arising from post-thermal treatment can be observed in Figure E8a. The assessed size of these nanoparticles is situated below the 10 nm threshold. The HR-TEM images of NiMo following the calcination process disclose exposed crystal planes characterized by a lattice spacing of

In-situ Design of a Nanostructured Interface between NiMo and CuO Derived from Metal–Organic Framework for Enhanced Hydrogen Evolution in Alkaline Solutions 154

0.24 nm (shown in Figure E8b). This feature corresponds to the (111) plane of NiO, aligning favorably with the XRD findings—affirming NiO as the predominant phase.

The TEM micrographs of NiMo/Cu-BDC before the calcination process reveal the presence of slender polygonal layers of Cu-BDC when subjected to the incident electron beam. These smooth layers presented in Figure E9a, forming stacked arrangements, exhibit lateral dimensions in the range of a few hundred nanometers, as corroborated by SEM results. HR-TEM photographs unveil the existence of numerous nanoscale particles situated along the edge of some nanosheet layers, confirming the construction of the nanosheets through the aggregation of these diminutive constituents (see Figure E9b).

Furthermore, the TEM image depicted in Figure E10 pertains to CuO derived from the Cu-BDC MOF, comprising nanosheets and nanoparticles. The measured lattice spacing of 0.25 nm matches with the respective crystallographic plane of ($\bar{1}11$) within the monoclinic CuO structure. The inset images displayed in Figure E10a and Figure 7. 3e illustrate the SAED patterns of Cu-BDC_{Cal.} and NiMo/Cu-BDC_{Cal.} along the zone axes [101] and [$\bar{2}01$], respectively, verifying the formation of a monoclinic CuO structure. Evidencing the interface between NiO nanoparticles (originated from NiMo) and CuO following the calcination process, HR-TEM images within Figure 7. 3e (refer to third and fourth images from left to right) distinctly showcase the interfacial region, characterized by discernible interplanar spacings of 0.24 nm corresponding to the (111) plane of NiO and 0.25 nm associated with the ($\bar{1}11$) plane of CuO. It is pertinent to underscore that HAADF-STEM images of NiMo/Cu-BDC_{Cal.} (Figure 7. 3f) confirm the presence of constituent elements including Cu, Ni, Mo, O, and C. Notably, the observed hollow carbonaceous structures in these images are indicative of encapsulating CuO, forming a CuO@C composite configuration.

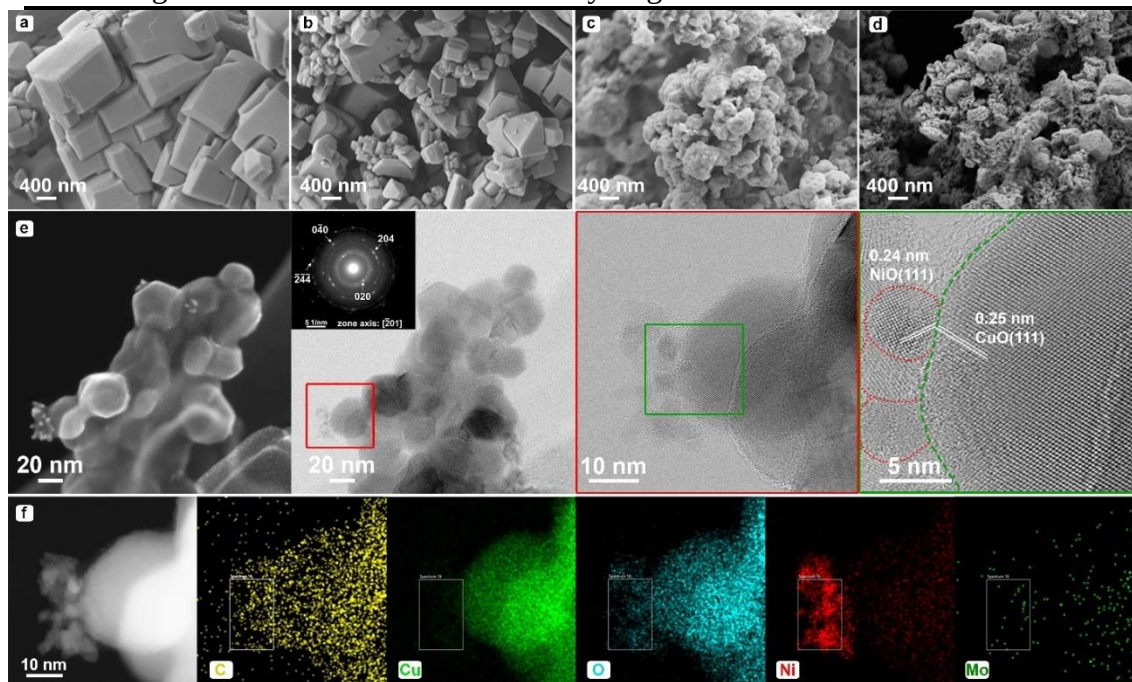


Figure 7. 3. Morphological and microstructural characterizations. SEM images of a) Cu-BDC, b) NiMo/Cu-BDC, c) Cu-BDC_{Cal.}, d) NiMo/Cu-BDC_{Cal.}, e) STEM, TEM, and HR-TEM images of NiMo/Cu-BDC_{Cal.} (inset: SAED pattern), and f) HAADF-STEM image and the corresponding EDS–STEM mappings of NiMo/Cu-BDC_{Cal.}.

To gain a deeper understanding of the surface composition and chemical states of the electrodes fabricated on the NF, XPS analysis was conducted. The XPS survey spectra of both NiMo/Cu-BDC and NiMo/Cu-BDC_{Cal.}, as depicted in Figure 7. 4, provided confirmation of the presence of elements including Cu, Ni, Mo, C, and O. In Figure 7. 4a, the XPS spectrum of Cu 2p prior to heat treatment revealed a well-fitted representation of the Cu 2p_{3/2} and Cu 2p_{1/2} spin-orbit splitting doublets, featuring distinct peaks at 934.67 eV and 954.03 eV, which correspond to the Cu²⁺ state.[298] Subsequent to the calcination process, the Cu 2p spectrum for NiMo/Cu-BDC_{Cal.} (Figure 7. 4b) exhibited a transformation into two doublets with spin-orbit values exceeding 19.5 eV. This transformation indicated the coexistence of both Cu⁺ and Cu²⁺ oxidation states, signifying a partial reduction of Cu²⁺ to Cu⁺ following thermal treatment.[299] This phenomenon was also observed in pristine Cu-BDC (see Figure E11). Notably, the atomic ratios of Cu 2p_{3/2} to Cu 2p_{1/2} for both cases after heat treatment were approximately 0.5.

In the C 1s region of pre-calcined NiMo/Cu-BDC, three distinct peaks at 284.5 eV (atomic % = 29.26), 285.91 eV (atomic % = 7.69), and 288.24 eV (atomic % = 27.04) eV were observed, corresponding to C=C/C–C, C–O, and C=O bonds, respectively. Subsequent to heat treatment, the C 1s core-level spectrum displayed three peaks at 284.5 eV (atomic % = 26.25), 286.01 eV (atomic % = 2.34), and 287.78 eV (atomic % = 3.28).

The peak that appeared at 284.5 eV is associated with graphitized carbon, which is the dominant carbon species after thermal treatment of the samples. The great attenuation of the peaks corresponding to C–O, and C=O in calcined samples compared to those before heat treatment indicates that most of the oxygen containing functional groups have been removed.[272, 300] This implies that CuO derived from Cu-BDC MOF may exhibit coordination with the carbon environment. Moreover, for both heat-treated catalysts, C 1s spectra shifted toward higher BEs, that is, electron is transferred from carbon to Cu and/or Ni/Mo. Hence, the transition metals are partially reduced and endowed with higher electron density and in turn larger number of available active sites for the adsorption of H^+ increases.[278] Finally, the O 1s spectra were analyzed, revealing three distinct peaks that confirmed the oxidation on the surface and in the crystal structure.[301]

The Ni 2p core-level XPS of NiMo/Cu-BDC revealed significant peaks at 854.47, 856.26, and 860.9 eV, corresponding to Ni^{2+} , Ni^{3+} , and an associated satellite, respectively.[266, 302] Following the calcination process, the Ni 2p spectrum exhibited the same oxidation states of 2+ and 3+ but exhibited a minor shift toward lower BEs, 854.23, 856.08, and 861.31 eV. It can be concluded that the transition metals were subjected to reduction during heat treatment process. Eventually, Figure 7. 4a,b showcased the Mo 3d region for NiMo/Cu-BDC before and after calcination. Prior to calcination, two sets of doublet pairs were observed at BEs 232.24 eV, 235.59 eV and 233.03 eV, 236.38 eV. These doublet pairs were attributed to the Mo^{4+} and Mo^{6+} oxidation states, respectively. The sample subjected to heat treatment exhibited the same oxidation states in the Mo 3d spectrum, albeit with a slight shift in BE toward lower values.[52]

7.3.2. *Electrocatalytic Studies*

The prepared electrodes were employed for electrocatalytic HER in 1.0 M KOH aqueous solution at ambient temperature. The LSV curves of fabricated samples along with commercial Pt/C, Cu-coated NF, and NF are shown in Figure 7. 5a. The overpotential at 10 mA cm^{-2} is an index to assess the HER performance of the samples (Figure 7. 5b). As expected, Pt/C electrode reached 10 mA cm^{-2} at low overpotential of 83 mV. Among the developed electrodes in this study calcined NiMo/Cu-BDC electrode afforded the 10 mA cm^{-2} at an overpotential as low as 85 mV which is almost identical to that of commercial Pt/C and smaller than that of NiMo/Cu-BDC (126 mV), Cu-BDC_{Cal}.

(219 mV), NiMo (256 mV), and pristine Cu-BDC (258 mV). Both Cu-BDC_{Cal.} (CuO@C) and calcined NiMo (almost NiO phase) did not show very high activity toward alkaline HER. However, their composite product illustrated HER performance similar to Pt/C at low overpotentials. The HER kinetics for the as-prepared samples were measured using corresponding Tafel plots derived from LSVs (Figure 7. 5c). Surprisingly, the best-performing sample exhibited a Tafel slope as high as 290 mV dec⁻¹ which is higher than those of Pt/C (105 mV dec⁻¹), NiMo/Cu-BDC (213 mV dec⁻¹), NiMo (200 mV dec⁻¹), Cu-BDC_{Cal.} (173 mV dec⁻¹), and pristine Cu-BDC (172 mV dec⁻¹). All the decisive parameters that can adversely affect Tafel slope were discussed in our recent publication.[278] The notable performance of best-performing HER catalyst can be attributed to i) high electrical conductivity of Cu-containing species within the sample, ii) the accelerated electron transfer due to the formation of an interface between the two components, iii) the electronic redistribution on the catalyst surface as a result of presence of elements with different electronegativity on the Pauling scale, Cu (1.9), Ni (1.91), Mo (2.16), O (3.44), and C (2.55).

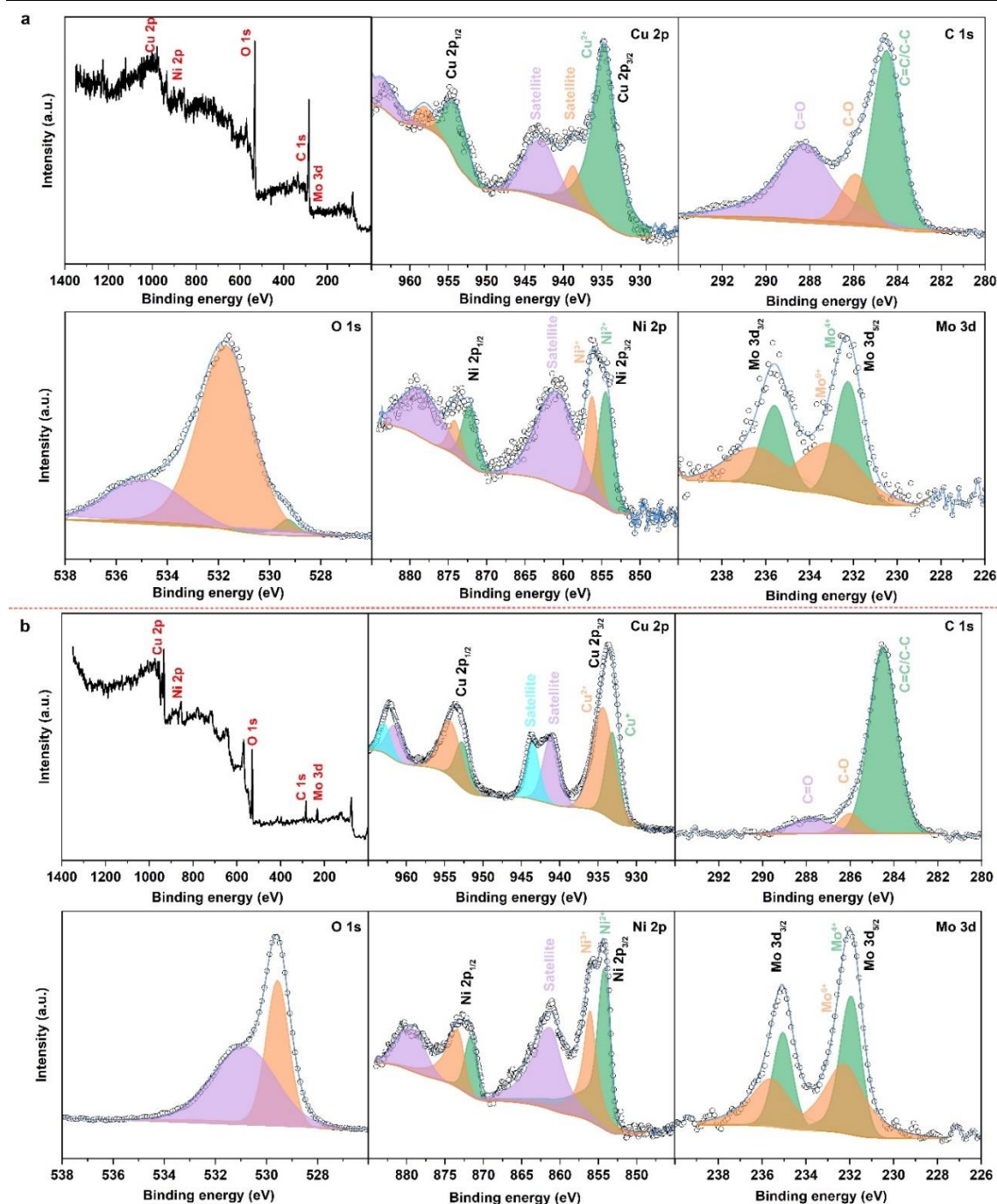


Figure 7. 4. XPS spectra including survey, Cu 2p, C 1s, O 1s, Ni 2p, and Mo 3d for a) NiMo/Cu-BDC and b) NiMo/Cu-BDC_{Cal.}.

As reported in previous studies, under alkaline conditions, the kinetics of the HER is elucidated by the adsorption/desorption processes involving hydrogen atoms/molecular hydrogen, employing either Volmer-Heyrovsky ($120\text{-}40\text{ mV dec}^{-1}$) or Volmer-Tafel ($120\text{-}30\text{ mV dec}^{-1}$) mechanisms.[17, 303] It is widely acknowledged that the HER kinetics is facile, unaffected by the specific defined overpotential of the catalyst. Thus, it can be confirmed that the HER kinetics demonstrate a remarkably uniform behavior

across all documented catalysts. Therefore, the rate determining step (RDS) for the as-prepared electrodes is through Volmer mechanism. Another crucial factor used to evaluate the inherent electrocatalytic performance of materials at the reversible overpotential ($\eta = 0$) is referred to as the exchange current density (j^0), which can be derived by extending the linear segment of the Tafel plot. The exchange current density is a parameter more commonly employed to assess the activity of the HER compared to its use in evaluating the OER. There is a direct correlation between the exchange current density and the onset overpotential in the HER.[301, 304] In other words, a catalyst is considered more active when its j^0 is higher. NiMo/Cu-BDC_{Cal.} exhibited a j^0 value of 5.84 mA cm^{-2} which is as twice as NiMo/Cu-BDC (2.64 mA cm^{-2}) and much higher compared to Cu-BDC_{Cal.} (0.3 mA cm^{-2}) and pristine Cu-BDC (0.31 mA cm^{-2}).

To further investigate the electrocatalytic performance, EIS experiment was carried out at -300 mV vs RHE to examine the catalytic kinetics, as portrayed in Figure 7. 5d. The semicircles could be found in the Nyquist plots, which are reference to the solution resistance (R_s), porosity resistance (R_p), and charge transfer resistance (R_{ct}). NiMo/Cu-BDC_{Cal.} showed R_{ct} around 2.6Ω , which is smaller than that of its counterparts, namely, NiMo/Cu-BDC (6.2Ω), Cu-BDC_{Cal.} (4.1Ω), and pristine Cu-BDC (7.2Ω). The data resulting from the fitting process was summarized in Table E1. Furthermore, the ECSA of the electrocatalysts were explored by calculating the C_{dl} according to the CV results (Figure E12) at different scan rates. From Figure 7. 5e, the results revealed that the NiMo/Cu-BDC_{Cal.} possesses higher C_{dl} (0.42 mF cm^{-2}) than NiMo/Cu-BDC (0.36 mF cm^{-2}), Cu-BDC_{Cal.} (0.33 mF cm^{-2}), and pristine Cu-BDC (0.3 mF cm^{-2}), manifesting larger active surface areas and abundant active site numbers for the NiMo/Cu-BDC_{Cal.}.

To compare the electroactive surface area with specific surface area, the BET surface area and pore volume of the selected samples were measured from N_2 adsorption-desorption isotherms (Figure E13). The effective BET surface area (pore volume) of the pristine Cu-BDC, Cu-BDC_{Cal.}, NiMo/Cu-BDC, and NiMo/Cu-BDC_{Cal.} were measured to be $146.88 \text{ m}^2/\text{g}$ ($0.061 \text{ cm}^3/\text{g}$), $4.26 \text{ m}^2/\text{g}$ ($0.001 \text{ cm}^3/\text{g}$), $122.74 \text{ m}^2/\text{g}$ ($0.049 \text{ cm}^3/\text{g}$), and $14.37 \text{ m}^2/\text{g}$ ($0.0009 \text{ cm}^3/\text{g}$), respectively. As expected, and explained in Introduction Section, when MOFs are exposed to high temperature, the degradation or decomposition of the porous structure can be conceived, leading to the framework collapse and dramatic decline in surface area. Additional specifics obtained from the BET analysis were summarized in Table E2. Besides the catalytic activity, the electrocatalytic durability of

NiMo/Cu-BDC_{Cal.} was evaluated by chronopotentiometry at -30 mA cm^{-2} in 1.0 M KOH. The catalyst showed no significant decrease in overpotential for 50 h (Figure 7. 5e), implying its practical long-term durability for the HER. The slight fluctuation of the long-term HER plot is due to the generation of hydrogen bubbles during the reaction.[272, 305] The catalytic activity for the post-HER durability was assessed through polarization curves, showing that catalytic performance drastically declined from 85 mV to 170 mV at 10 mA cm^{-2} .

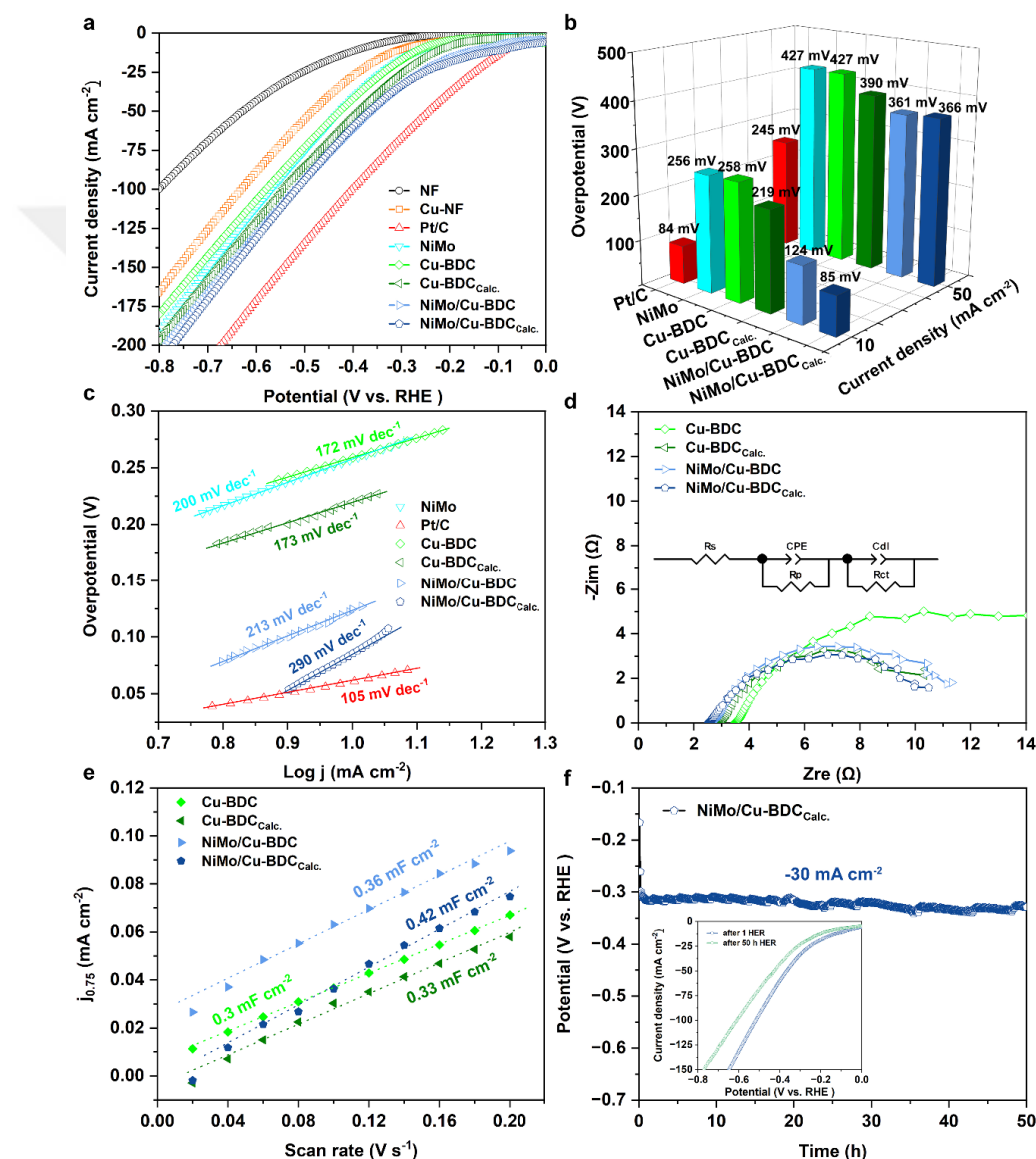


Figure 7. 5. Electrocatalytic hydrogen evolution performances in 1.0 M KOH. a) HER polarization curves of the samples, b) 3D bar graphs of overpotentials at 10 and 50 mA cm^{-2} , c) HER Tafel plots obtained by polarization curves, d) EIS spectra recorded at -300 mV versus RHE, e) Capacitive current density versus scan rate curves for ECSA measurements, and f) Long-term HER durability test of NiMo/Cu-BDC_{Cal.} at an applied current density of -30 mA cm^{-2} (inset: HER polarization curves of NiMo/Cu-BDC_{Cal.} before and after long-term HER).

7.3.3. *Post-electrocatalysis Characterization*

To examine the alterations on the electrode after 50 h HER experiment, the post-electrolysis characterizations including SEM, TEM/HR-TEM, and XPS studies were carried out. The SEM images of the HER electrode before and after measurement displayed a distinct difference. The spherical particles tightly stuck to one another, forming big chunks of materials on the NF (refer to high-magnified SEM image in Figure 7. 6a). Therefore, the porous structure observed before measurement almost disappeared after long-term HER (refer to low-magnified SEM image in Figure E6d). The TEM/HR-TEM micrographs demonstrated similar morphology for the used sample after long-term durability test, showcasing nanoparticles and nanosheets within the sample batch. From Figure 7. 6b, the dense agglomeration of nanoparticles after stability measurement is discernible with the darker region in the TEM images surrounded by comparatively lighter region. XPS results showed that the transition metals including Cu, Ni, and Mo moved to the lower binding energies compared to the initial sample. Interestingly, for the Cu 2p XPS core spectrum, the Cu^+ shifted to higher BEs, while Cu^{2+} shifted to lower BEs. In addition, the valence states of Mo 3d changed, transforming into only Mo^{4+} oxidation state, eliminating Mo^{6+} . It can be concluded during long-term HER, Ni 2p and Cu 2p were electrochemically stable. On the contrary, Mo 3d was not completely stable during 50 h HER operation (see Figure 7. 6c). The comparison of atomic proportions for the best-performing HER electrode before and after stability test revealed that C 1s and O 1s remained almost unchanged. In sharp contrast, transition metals such as Cu 2p (12. 27% $\rightarrow$ 7.83%), Ni 2p (5.71% $\rightarrow$ 1.8%), and Mo 3d (1.78% $\rightarrow$ 0.11%) dramatically declined after 50 h HER test. These findings suggested that transition metals in the framework of catalyst were the favorable active sites for the adsorption of H^+ and its subsequent evolution to H_2 .

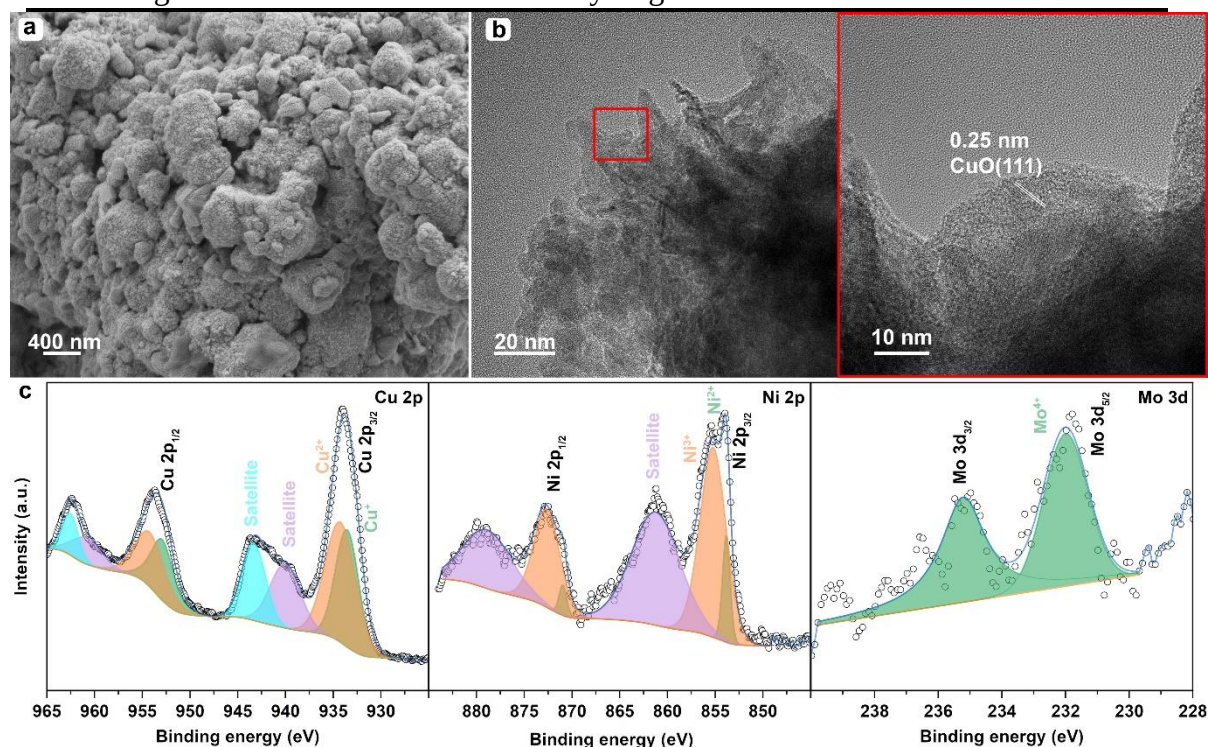


Figure 7. 6. Post-electrolysis characterizations of NiMo/Cu-BDCCal. after long-term HER test. a) SEM image, b) TEM and HR-TEM images, and c) XPS Cu 2p, Ni 2p, and Mo 3d.

7.4. Proposed Mechanism

The superior HER performance of NiMo/Cu-BDCCal. should be attributed to the synergy between the high charge mobility of carbon layer formed at high temperature, the charge flow between NiO —originated from NiMo— and CuO via the in-situ formed interface, and the catalytically active metal sites. The co-existence of metallic Cu (electrodeposited on the NF) and carbon layer establishes a conductive network for the rapid charge flow in the redox reaction. Moreover, carbon layer could effectively reduce the dense aggregation of metal oxides during high-temperature process, creating porous structure for better contact with water and detachment of bubbles.[272, 282] The close contact between carbon layer and NiO/CuO facilitates the electron transfer to the catalytically active metal sites. Based upon XPS results, both NiO and CuO possess partially negative charges after the coupling of two components (refer to XPS interpretation, Figure 7. 4). Hence, the charges flow from carbon layer to NiO and CuO, resulting in higher electron density on Ni and Cu. NiO_x has been shown to play a vital role in the HER process.[306-308] It is proved that transition metal oxides are not suitable catalysts for transforming the H⁺ to H₂.[309] Yet, it is proposed that the dissociation of

water (H^+/OH^-) is more favorable on metal oxides (more favorable Volmer kinetics), on the other hand, H_2 is more readily formed on metallic surface.[278] Considering the Tafel slopes, which are above 120 mV dec^{-1} , the HER is primarily governed by a Volmer step, followed by a Heyrovsky step. As illustrated in Figure 7. 7, in the first step, interactions—that are, electrostatic attraction between $\text{Cu}^{\delta+}/\text{Ni}^{\delta+}$ on the catalyst surface with O^{2-} ions, along with the interaction between $\text{O}^{\delta-}$ on the catalyst surface with H^+ ions, facilitate the adsorption of H_2O and weaken the $\text{H}-\text{O}-\text{H}$ bond, leading to the dissociation of adsorbed H_2O into OH^- and H^+ ions. In the second step, the generated OH^- ions, resulting from the dissociation of water, coordinate with $\text{Cu}^{\delta+}/\text{Ni}^{\delta+}$ ions in the vicinity of oxygen (O), while H^+ ions adsorbed (ads) on $\text{O}^{\delta-}$ ions may undergo surface diffusion—that is, they can move along the surface of the crystal lattice, hopping from one adsorption site to another and transfer to nearby $\text{Cu}^{\delta+}/\text{Ni}^{\delta+}$ ions. The adsorption of another water molecule and the combination of two H^+ ions result in the formation of molecular H_2 .

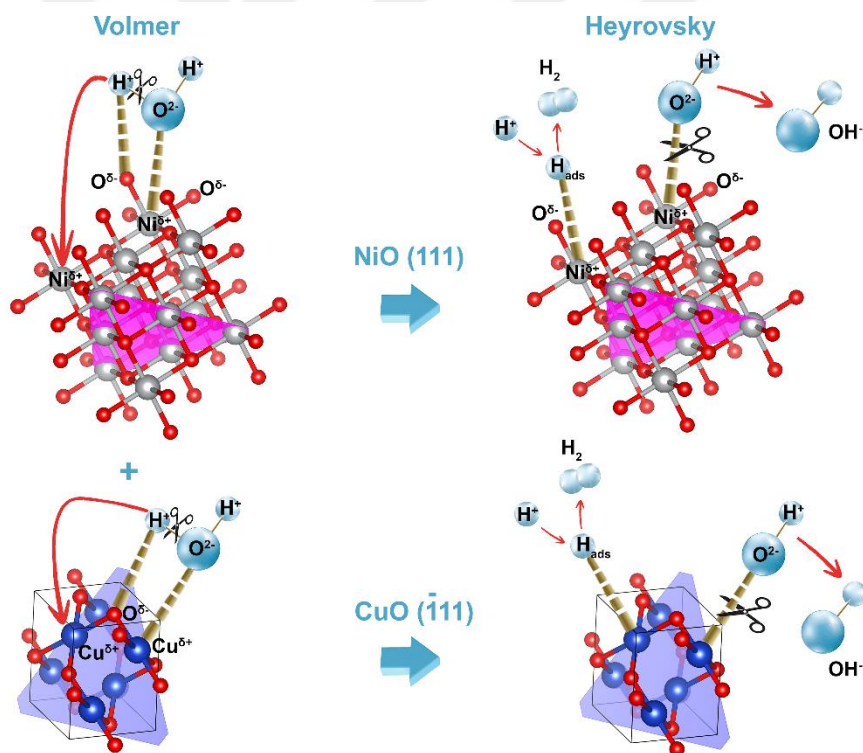


Figure 7. 7. Schematic presentation of proposed HER mechanism.

7.5.CONCLUSIONS

In brief, a nanocomposite electrocatalyst, NiO/CuO@C derived from NiMo/Cu-BDC MOF, was fabricated on Cu-coated NF through hydrothermal procedure followed by calcination under air. The TEM and HR-TEM micrographs revealed formation of a

tight nanostructured interface between NiO (originated from NiMo) and CuO (derived from Cu-BDC). This can expose the active metallic sites, alleviate the adsorption of intermediates (H^+/OH^-), and boost the diffusion of ions. Moreover, the carbon layer could improve the charge transfer through the structure. Thus, the metals were endowed with higher electron density to adsorb the H^+ . Furthermore, the higher conductivity of the product led to lower charge transfer resistance on the electrode/electrolyte interface. The fabricated electrode afforded 10 mA cm^{-2} at a small overpotential of 85 mV toward hydrogen evolution in 1.0 M KOH solution. Finally, the chronopotentiometry experiment was carried out at -30 mA cm^{-2} for 50 h to evaluate the catalyst's long-term durability. This work can be used to develop cheap metal oxide nanocomposites that not only are active but also stable under high current densities.

CHAPTER 8

CONCLUSION

Over the course of four intensive years of research, this thesis has been dedicated to pushing the boundaries of electrocatalysis in the context of electrochemical water splitting. As the world grapples with the escalating challenges of environmental sustainability and a burgeoning global population, the pursuit of an alternative, sustainable energy source to replace fossil fuels has taken on unparalleled significance. It is within this context that we embarked on a journey to explore the integration of renewable energy resources with electrocatalytic water splitting, with a focus on developing electrocatalysts that are not only earth-abundant but also cost-effective and highly efficient in driving both the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) within the same electrolyte.

Our research endeavors have led to notable contributions across various dimensions:

1. Novel Electrocatalysts: In our first pursuit, we harnessed a straightforward, scalable method to synthesize a series of novel metal-doped MgB_2 materials featuring earth-abundant elements, specifically Fe and Co. These catalysts were extensively evaluated for their performance in both the HER and OER, particularly under the conditions of 1.0 M KOH. Among these catalysts, $\text{Mg}_{0.95}\text{Co}_{0.05}\text{B}_2$ emerged as a standout performer in HER, displaying an overpotential of 470 mV at 10 mA cm^{-2} , thanks to its optimal charge transfer characteristics and fast electron transport. Simultaneously, our investigation unveiled that Fe content and overpotential for HER have an inverse relationship, with the highest Fe doping concentration ($x = 0.1$) yielding the lowest overpotential. This comprehensive electrochemical study underscores the potential of developing highly efficient, low-cost electrocatalysts composed of readily available precursors, while also introducing a facile scalable method for the assembly of highly porous electrodes, setting the stage for future breakthroughs in the field.

2. Transformative Materials: Our exploration led us to develop Co-substituted VB_2 materials, showcasing the power of morphological transformation induced by Co substitution. In particular, $\text{V}_{0.9}\text{Co}_{0.1}\text{B}_2$ exhibited remarkable OER activity, requiring only

200 mV to achieve a current density of 10 mA cm^{-2} , rivaling the performance of the noble-metal catalyst RuO_2 . This transformation in morphology, characterized by an increase in catalytically active sites, was confirmed by electrochemical surface area analysis. The significant gains in OER performance and the catalyst's notable durability under 1.0 M KOH conditions open up new avenues for practical OER electrocatalysts.

3. Metal Organic Frameworks (MOFs): In our third endeavor, we ventured into the realm of nanocomposites based on NCM/Ni-BDC@NF, directly synthesized on NF. These nanocomposites revealed intriguing electronic structure modulation, leading to a unique set of performance characteristics. Notably, NCF/Ni-BDC displayed outstanding OER performance, with the ability to reach 10 mA cm^{-2} current density at an impressively low potential of 1.35 V versus a reversible hydrogen electrode. In contrast, NCZ/Ni-BDC excelled in HER activity, offering overpotentials of 170 and 350 mV for 10 and 50 mA cm^{-2} , respectively, under 1.0 M KOH. These materials were then brought together in a two-electrode alkaline electrolyzer, where the NCZ/Ni-BDC || NCF/Ni-BDC coupling demanded a mere 1.58 V cell voltage to achieve a 10 mA cm^{-2} current density. This performance surpassed the benchmark electrode couple of Pt/C || RuO_2 , underscoring the synergy between diverse factors, including the unique hierarchical architecture, electronic structure modulation, formation of multiple metal/metal oxide interfaces, and the creation of abundant active sites.

4. Heterostructures: In our fourth research dimension, we presented a high-performance and durable heterostructure of NiMo/CoMoO₄ for the alkaline HER. This structure, constructed via a two-pot in situ growth strategy on a NF, delivered an exceptional overpotential of 102 mV at 10 mA cm^{-2} , approaching the performance of platinum on carbon (83 mV) in 1.0 M KOH. The unique characteristics of this heterostructure, including the density of active sites, increased surface area, and the synergistic interaction between metallic NiMo and oxygen vacancy-confined CoMoO₄, facilitated the efficient adsorption of H and OH species, significantly enhancing the electrocatalyst's performance.

5. MOF-Derived Catalysts: In our final investigation, we unveiled the potential of a nanostructured interface between NiO/CuO@C, derived from NiMo/Cu-BDC MOF, as a competent HER electrocatalyst in alkaline media. This catalyst demonstrated a low overpotential of 85 mV at 10 mA cm^{-2} , rivaling the performance of Pt/C, and exhibited remarkable durability over an extended period of 50 h.

As we conclude this thesis, it is evident that our research journey has not only enriched our understanding of advanced electrocatalysts but has also advanced the prospects for sustainable water splitting, particularly for hydrogen production. These findings hold promise for a cleaner and more sustainable energy landscape.

The path ahead is marked by further exploration and innovation, with the goal of realizing the potential of these materials on a larger scale. As the global community strives for a more sustainable and eco-friendly energy future, the insights and innovations emerging from this research offer a glimpse into the possibilities that lie ahead. This thesis is a testament to our collective effort and dedication to making a meaningful impact in the world of clean energy and sustainable solutions. The journey continues, and the destination is a cleaner, brighter, and more sustainable future.



Appendix A

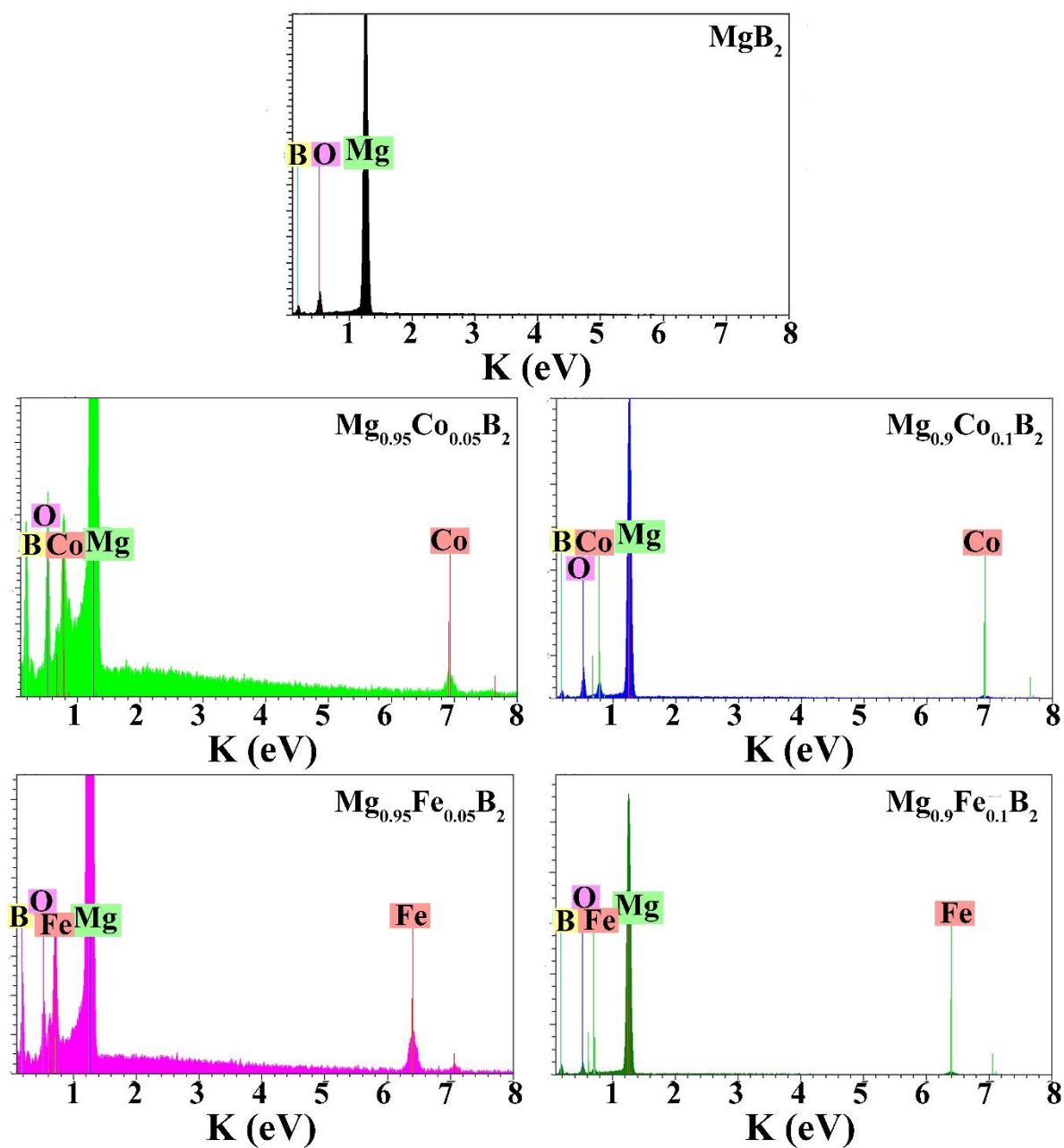


Figure A1. EDX analysis graph of pure MgB_2 and $\text{Mg}_{1-x}\text{Tm}_x\text{B}_2$ ($x = 0.05$, and 0.1 ; $\text{Tm} = \text{Fe}$ and Co) before electrochemical reactions.

Table A 1. Energy-dispersive X-ray spectroscopy (EDX) analysis of samples before HER and OER.

Sample	Element	atomic %	atomic %
MgB ₂	Mg	30.51	29.28
	B	69.49	63.26
	O	-	7.46
Mg _{0.95} Fe _{0.05} B ₂	Mg	26.65	26.12
	Fe	1.32	1.29
	B	72.03	69.58
	O	-	3.01
Mg _{0.95} Co _{0.05} B ₂	Mg	26.22	25.62
	Co	1.59	1.55
	B	72.19	69.20
	O	-	3.63
Mg _{0.9} Fe _{0.1} B ₂	Mg	27.20	26.63
	Fe	2.31	2.26
	B	70.49	67.99
	O	-	3.12
Mg_{0.9}Co_{0.1}B₂	Mg	31.45	29.54
	Co	3.23	3.00
	B	65.32	58.40
	O	-	9.06

Table A 2. Lattice parameters (a and c in the space group $P6/mmm$) of samples investigated.

Starting Composition	a (Å)	c (Å)
MgB₂	3.0832(3)	3.5187(5)
Mg_{0.975}Co_{0.025}B₂	3.0847(2)	3.5223(4)
Mg_{0.95}Co_{0.05}B₂	3.0864(2)	3.5241(3)
Mg_{0.9}Co_{0.1}B₂	3.0834(3)	3.5219(6)
Mg_{0.975}Fe_{0.025}B₂	3.0843(3)	3.5206(7)
Mg_{0.95}Fe_{0.05}B₂	3.0849(1)	3.5240(3)
Mg_{0.9}Fe_{0.1}B₂	3.0842(2)	3.5238(4)

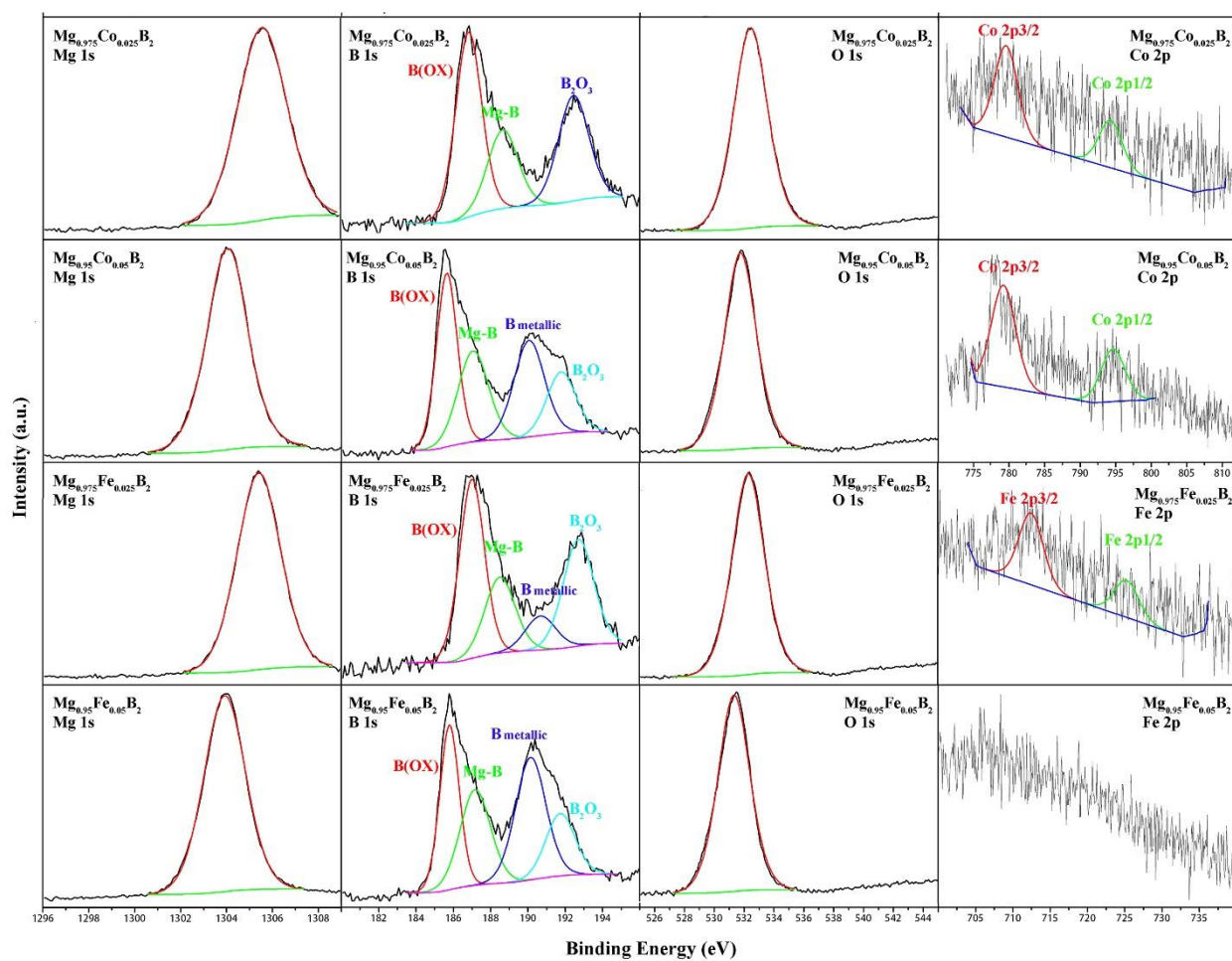


Figure A2. XPS spectra of Mg 1s, B 1s, O 1s, Co 2p, and Fe 2p in $\text{Mg}_{0.975}\text{Co}_{0.025}\text{B}_2$, $\text{Mg}_{0.95}\text{Co}_{0.05}\text{B}_2$, $\text{Mg}_{0.975}\text{Fe}_{0.025}\text{B}_2$, and $\text{Mg}_{0.95}\text{Fe}_{0.05}\text{B}_2$.

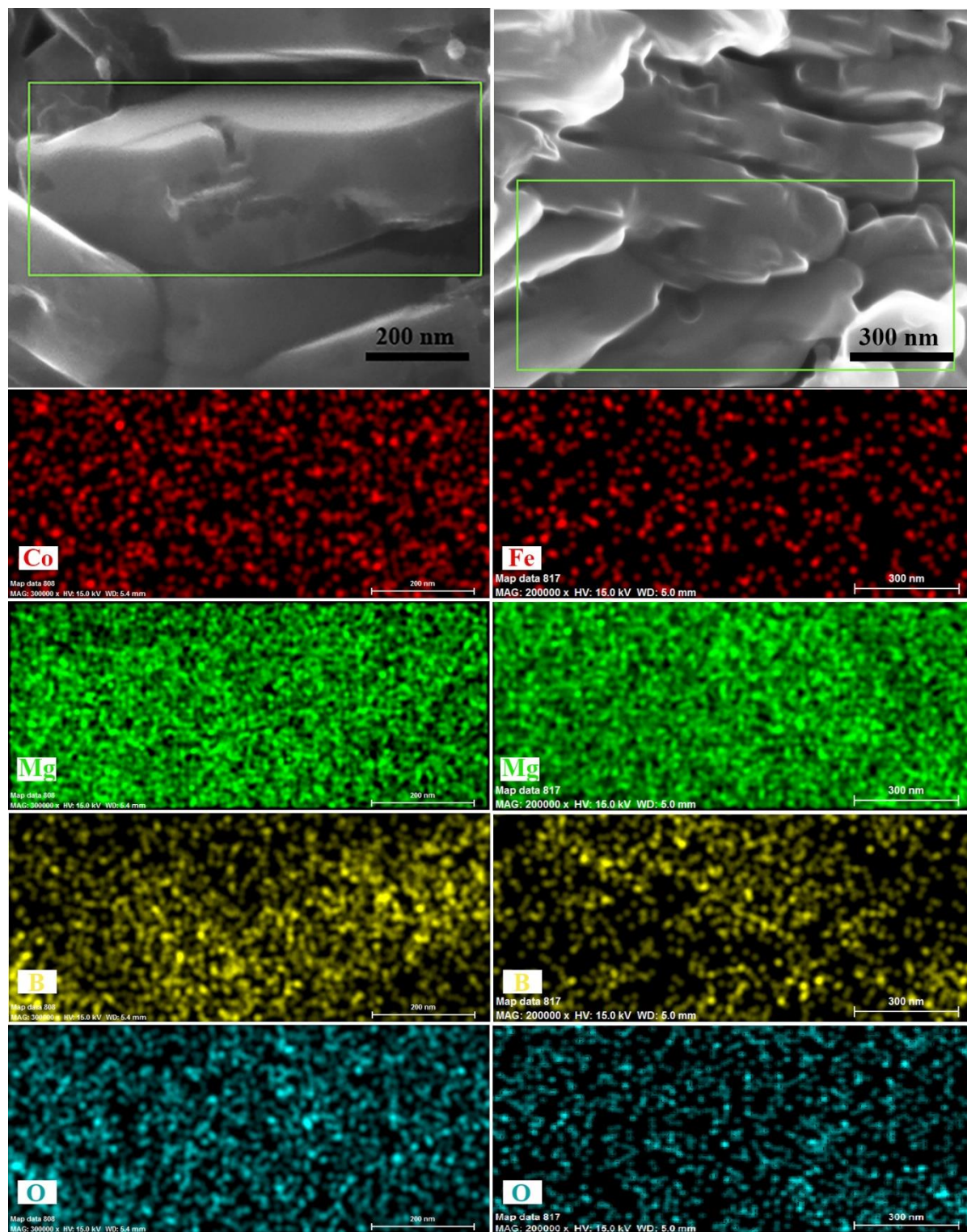


Figure A3. SEM images (15.0 kV HV) of $\text{Mg}_{0.95}\text{Co}_{0.05}\text{B}_2$ (left column) and $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{B}_2$ (right column) samples with corresponding elemental mappings.

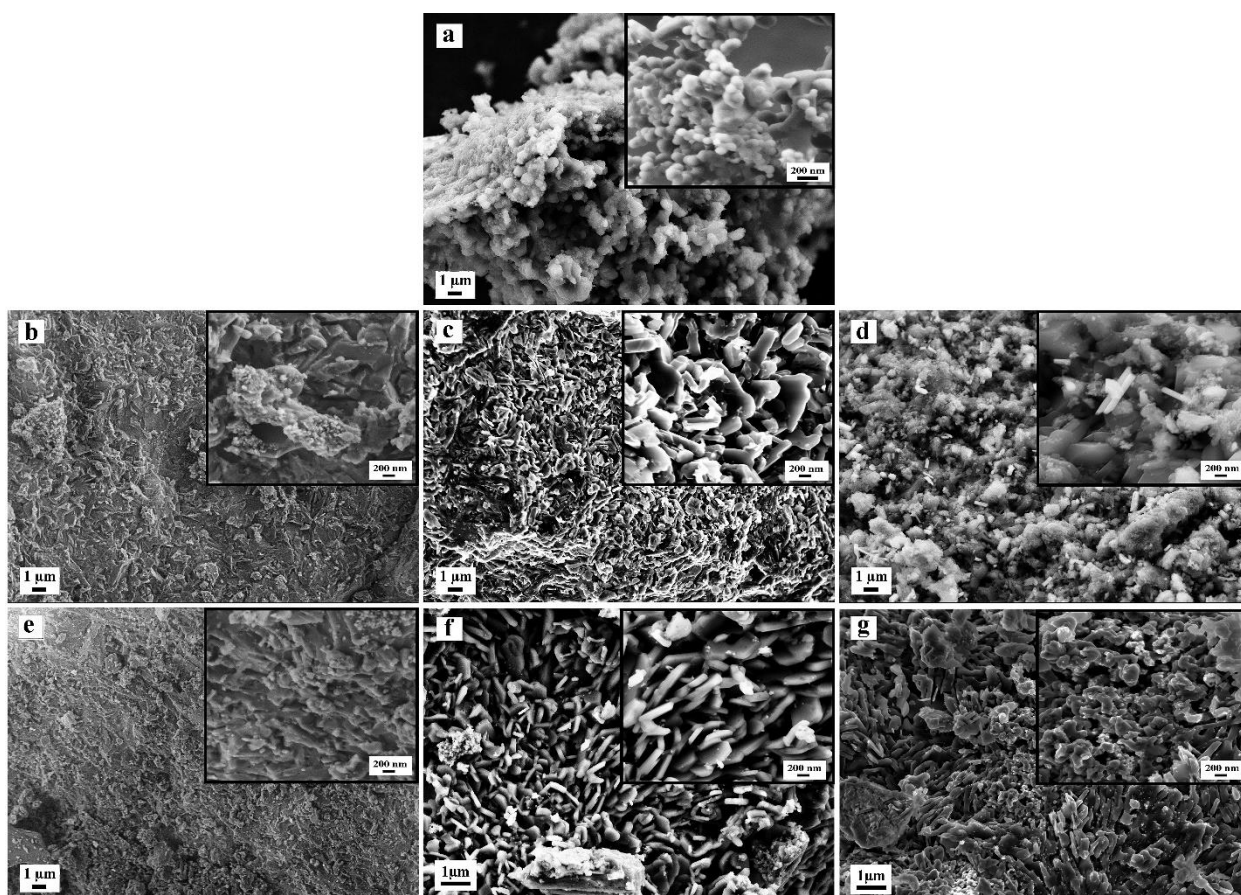


Figure A4. SEM images of a) pure MgB₂, b) Mg_{0.975}Co_{0.025}B₂, c) Mg_{0.95}Co_{0.05}B₂, d) Mg_{0.9}Co_{0.1}B₂, e) Mg_{0.975}Fe_{0.025}B₂, f) Mg_{0.95}Fe_{0.05}B₂, and g) Mg_{0.9}Fe_{0.1}B₂

Table A 3. Equivalent-circuit element values for EIS data in the 1 M KOH electrolyte.

	Re (Ωcm^{-2})	R1 ($\text{k}\Omega\text{ cm}^{-2}$)	CPE1-T ($\text{Fs}^{p-1}\text{ cm}^{-2}$)	CPE1-P	R2 ($\text{k}\Omega\text{ cm}^{-2}$)	CPE2-T ($\text{Fs}^{p-1}\text{ cm}^{-2}$)	CPE2-P
MgB ₂	130.5	10.993	2.5E-05	0.43	127.114	5.1E-05	0.56
Mg _{0.975} Co _{0.025} B ₂	12.2	1.436	4.5E-04	0.47	18.331	2.4E-04	0.72
Mg _{0.95} Co _{0.05} B ₂	13.6	0.409	1.3E-03	0.45	10.409	5.1E-04	0.66
Mg _{0.9} Co _{0.1} B ₂	13.2	3.539	3.4E-04	0.45	13.712	2.7E-04	0.71
Mg _{0.975} Fe _{0.025} B ₂	7.52	0.454	2.7E-04	0.36	710	1.5E-05	0.56
Mg _{0.95} Fe _{0.05} B ₂	13.5	0.277	3.4E-03	0.40	14.325	6.2E-04	0.67
Mg _{0.9} Fe _{0.1} B ₂	11.9	0.332	1.6E-03	0.45	7.980	1.2E-03	0.62

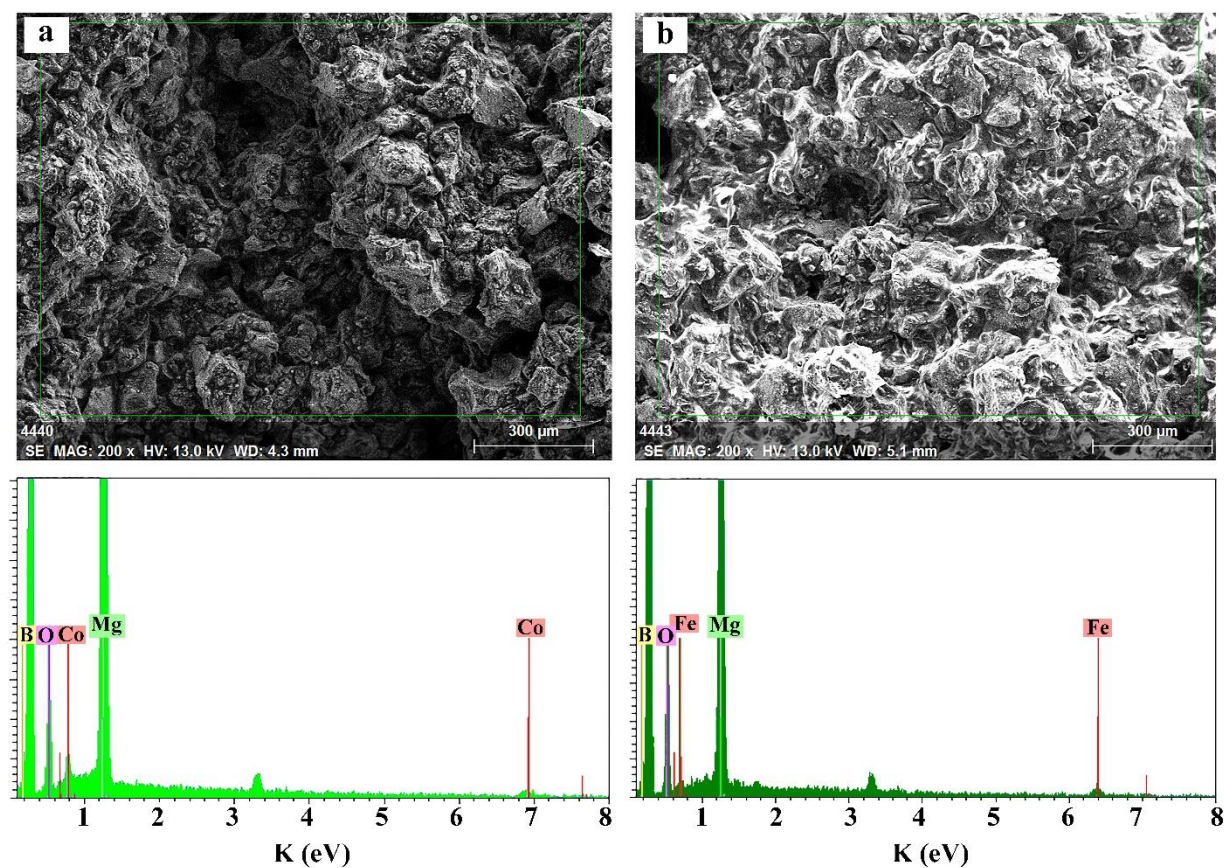


Figure A5. EDX results of the (a) $\text{Mg}_{0.95}\text{Co}_{0.05}\text{B}_2$ and (b) $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{B}_2$ after electrochemical reactions.

Table A 4. Energy-dispersive X-ray spectroscopy (EDX) analysis of the best-performing samples after HER and OER.

Sample	Element	atomic %	atomic %
$\text{Mg}_{0.95}\text{Co}_{0.05}\text{B}_2$	Mg	25.29	23.65
	Co	1.19	1.09
	B	73.52	64.68
	O	-	10.59
$\text{Mg}_{0.9}\text{Fe}_{0.1}\text{B}_2$	Mg	21.71	19.59
	Fe	1.64	1.48
	B	76.65	64.00
	O	-	14.93

Aside from catalytic activity, stability is another influential criterion. To appraise the cycling durability of the $\text{Mg}_{0.95}\text{Co}_{0.05}\text{B}_2$ and $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{B}_2$ electrodes, the cyclic voltammetry (CV) plots were measured within a potential range of -1 and -0.2 V for 1000 cycles at a scan rate of 50 mV s^{-1} . Fig. S6a and b demonstrate the reordered CV curves of $\text{Mg}_{0.95}\text{Co}_{0.05}\text{B}_2$ and $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{B}_2$ electrodes for the 1st and 1000th cycles in 1 M KOH electrolyte. As shown in the figure, it is obvious that after 1000 cycles the current density diminished for both electrodes. Even though the current density did not decrease appreciably, yet further investigations are needed to excel in the stability of these very new electrocatalysts.

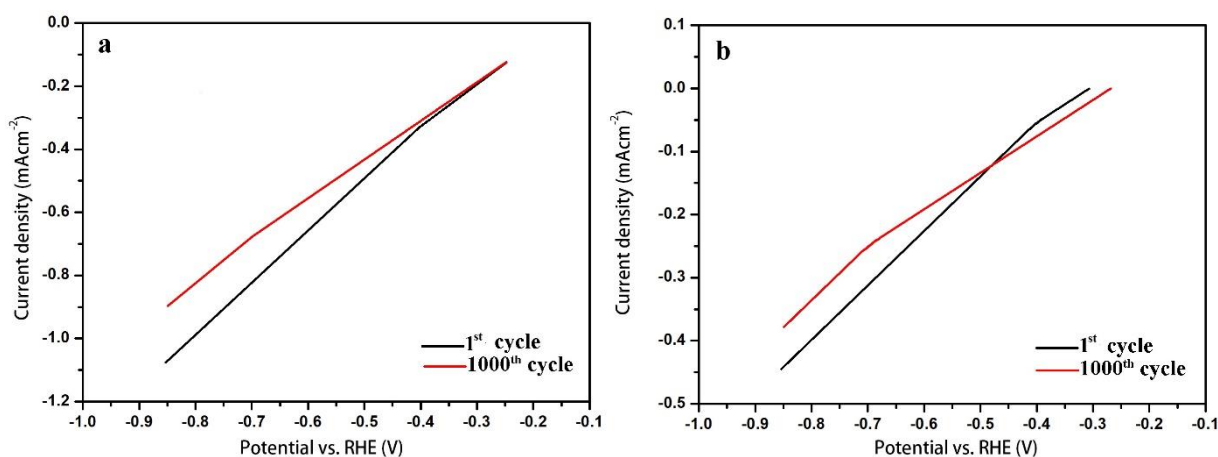


Figure A6. Electrochemical cycling stability measurement. a) and b) CV curves of $\text{Mg}_{0.95}\text{Co}_{0.05}\text{B}_2$ and $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{B}_2$, respectively, for 1st and 1000th cycles in a 1 M KOH electrolyte at a scan rate of 50 mV s^{-1} .

Appendix B

Collection efficiency (*N*) of that RRDE electrode

The collection efficiency, *N*, of the rotating ring-disk electrode (RRDE) was determined by the ratio of the ring limiting current to the disk limiting current through the relation written below in 0.001 M K₃Fe(CN)₆ containing 0.3 M of KOH following the previously reported procedure[310]:

$$N = \frac{i_{\text{Limiting, ring}}}{i_{\text{Limiting, disk}}} \quad (\text{Equation B1})$$

At disk electrode, the reduction of ferricyanide (Fe(CN)₆³⁻) to ferrocyanide ((Fe(CN)₆⁴⁻) took place, on the other hand, ferrocyanide is oxidized to ferricyanide at ring at positive potential (0.7 V vs. Ag/AgCl). The value of *N* was calculated at 1600 rpm to be 0.84.

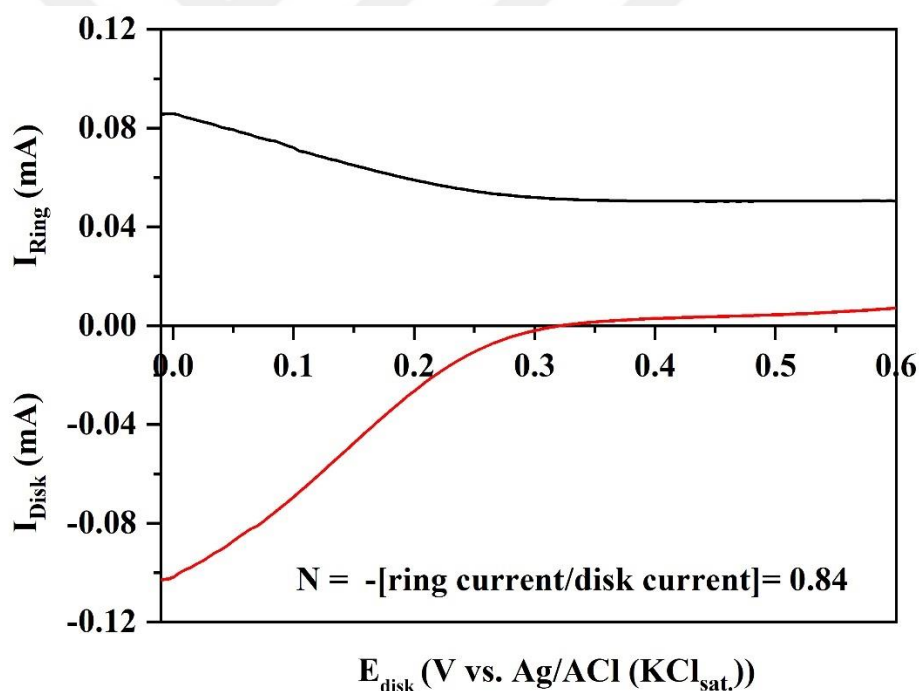


Figure B1. Rotating Ring-Disk voltamograms in N₂-saturated 0.001 M K₃Fe(CN)₆ containing 0.3 M of KOH at 0.05 V s⁻¹ and 1600 rpm. Ring potential was held on 0.7 V vs. Ag/AgCl which is sufficient to oxidize the product rapidly at ring.

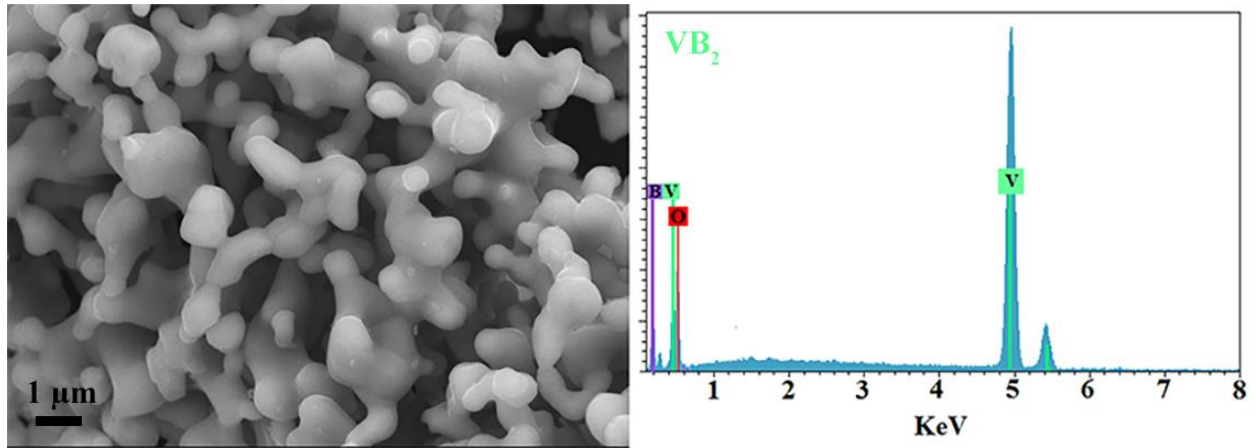


Figure B2. SEM image and corresponding EDS elemental analysis graph of VB_2 .

Table B 1. EDS elemental composition of $\text{V}_x\text{Co}_{1-x}\text{B}_2$ ($x = 0, 0.05, 0.1, \text{ and } 0.2$) with and without oxygen.

Sample	Element	atomic % (without oxygen)	atomic % (with oxygen)
VB_2	V	27.48	24.03
	B	72.52	65.35
	O	-	10.63
$\text{V}_{0.95}\text{Co}_{0.05}\text{B}_2$	V	28.44	22.67
	Co	1.57	1.27
	B	69.99	56.63
	O	-	19.43
$\text{V}_{0.9}\text{Co}_{0.1}\text{B}_2$	V	26.34	21.95
	Co	3.58	3.04
	B	70.08	59.02
	O	-	15.99
$\text{V}_{0.8}\text{Co}_{0.2}\text{B}_2$	V	24.98	21.29
	Co	6.29	5.38
	B	68.73	59.15
	O	-	14.18

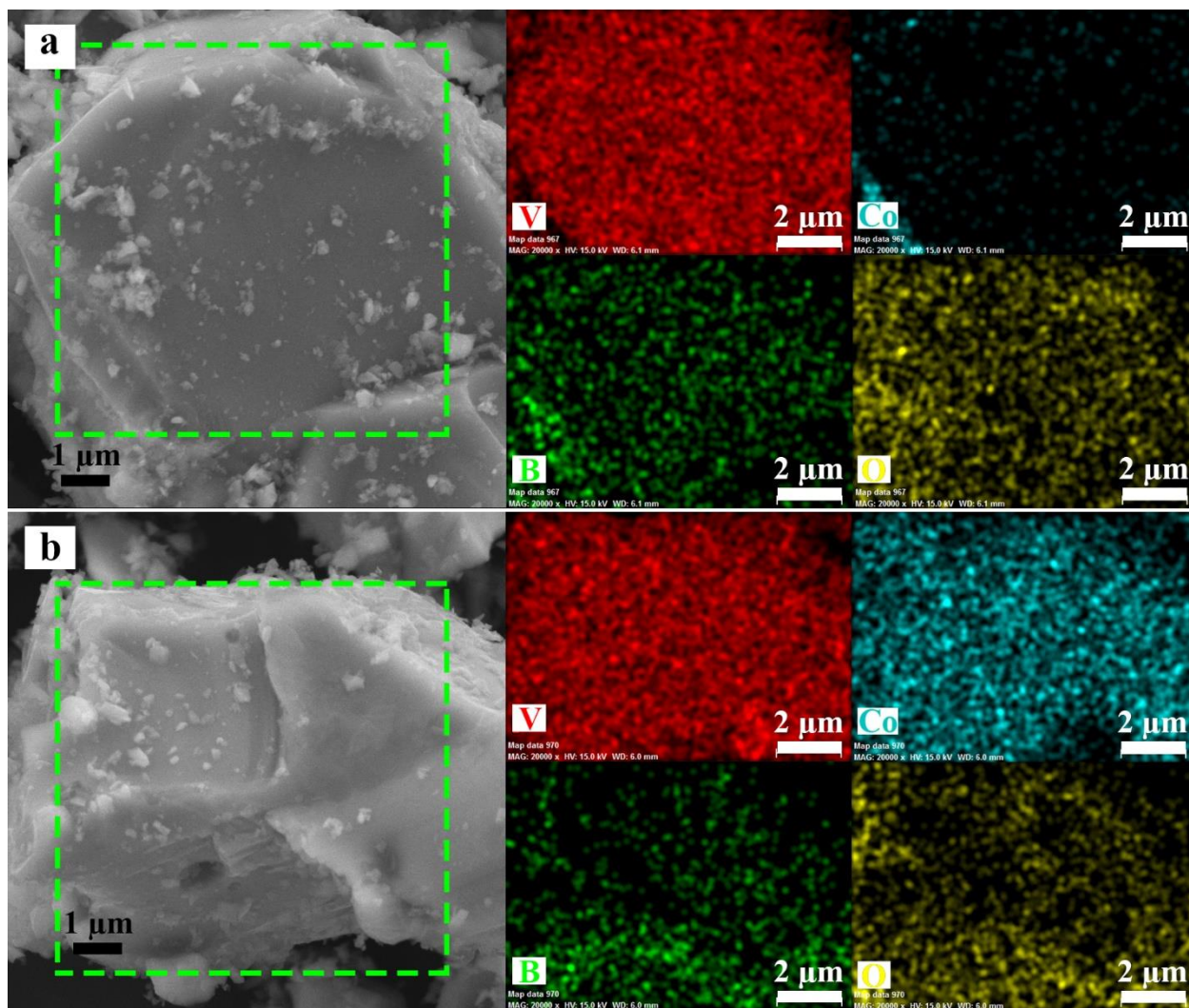


Figure B3. High magnification SEM images and corresponding EDS elemental mapping of (a) $V_{0.95}Co_{0.05}B_2$ (b) $V_{0.8}Co_{0.2}B_2$

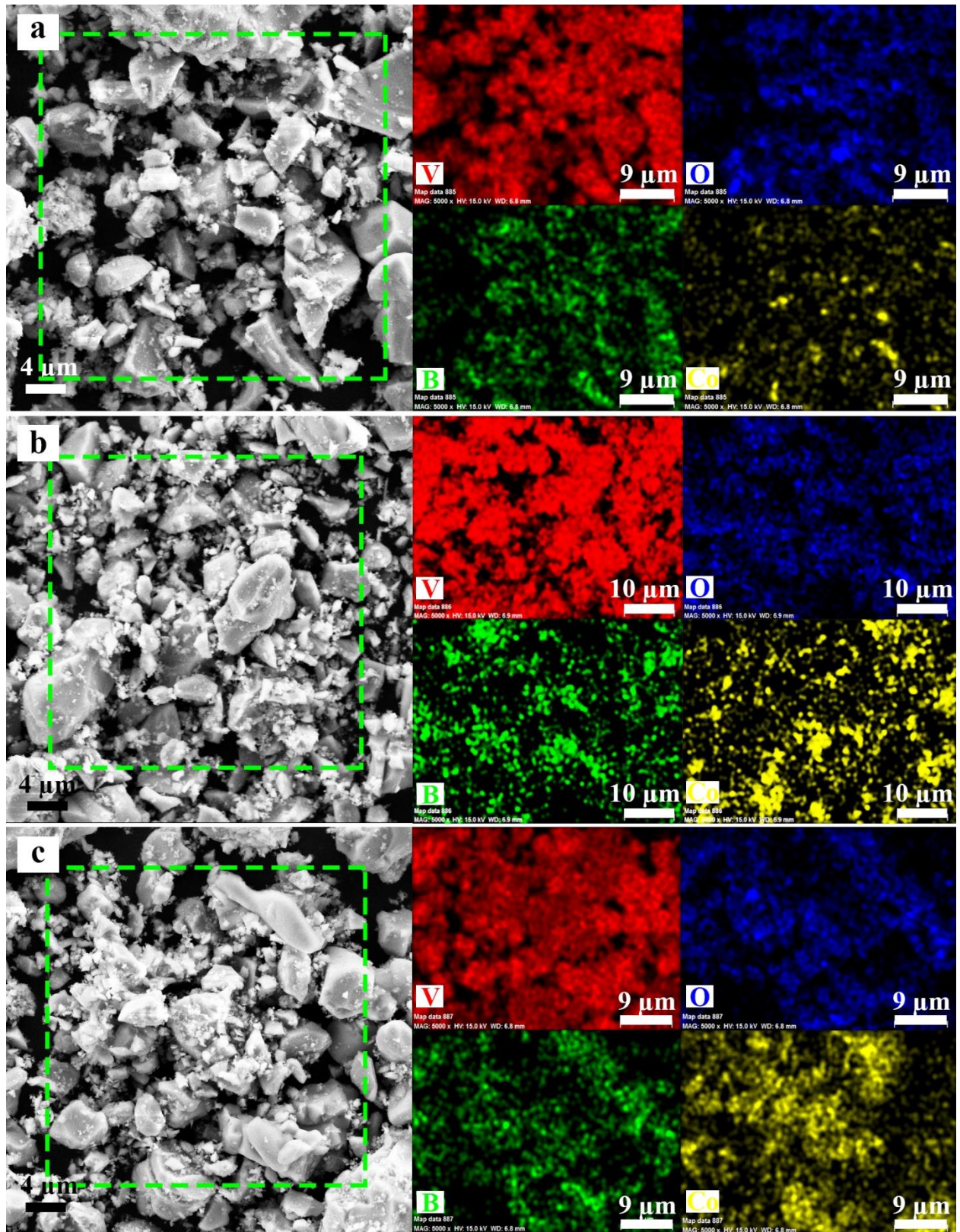


Figure B4. Low magnification SEM images and corresponding EDS elemental mapping of (a) $V_{0.95}Co_{0.05}B_2$ (b) $V_{0.9}Co_{0.1}B_2$ (c) $V_{0.8}Co_{0.2}B_2$

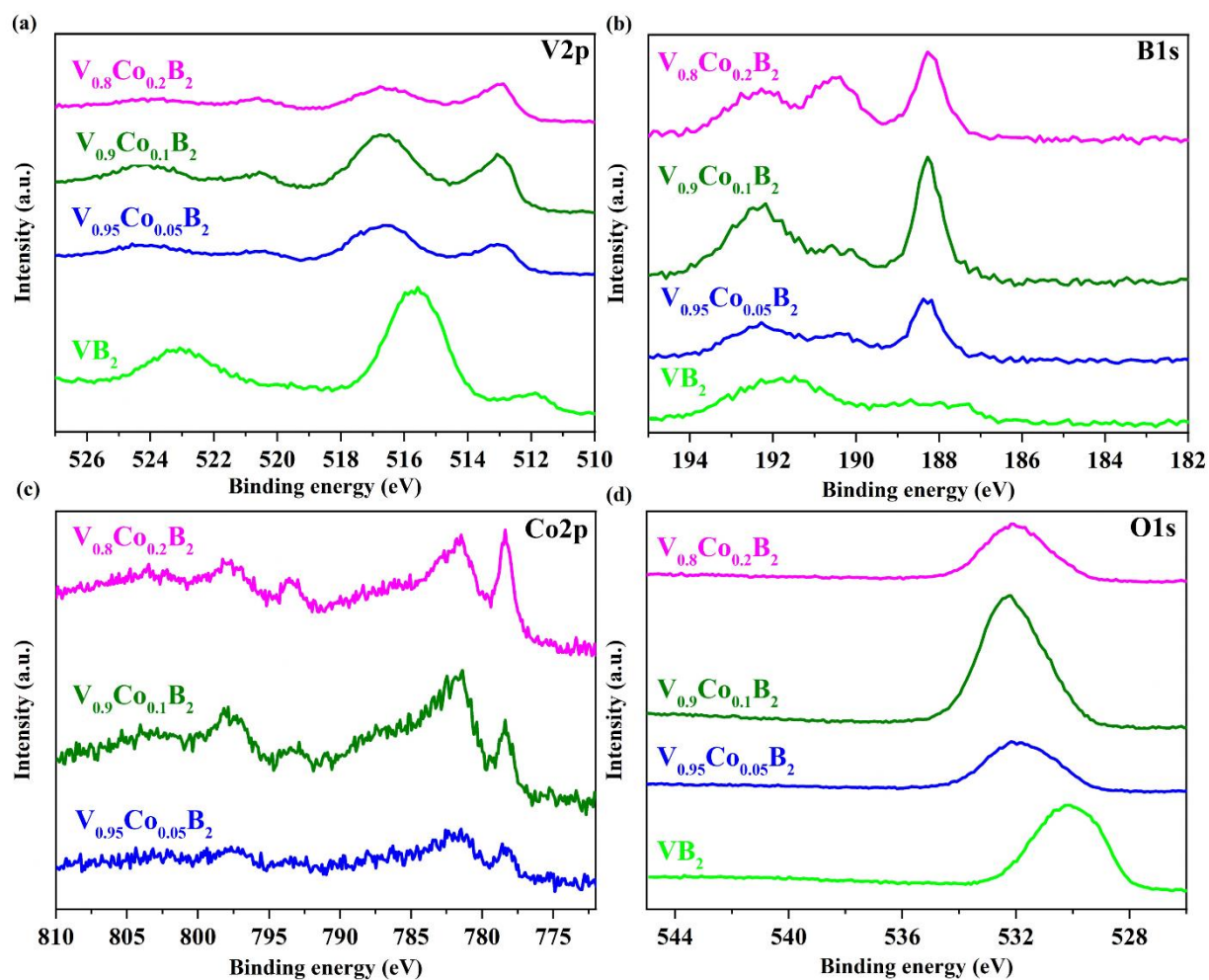


Figure B5. High-resolution XPS spectrum of (a) V 2p (b) B 1s (c) Co 2p (d) O 1s for $V_{1-x}Co_xB_2$ ($x = 0, 0.05, 0.1$, and 0.2)

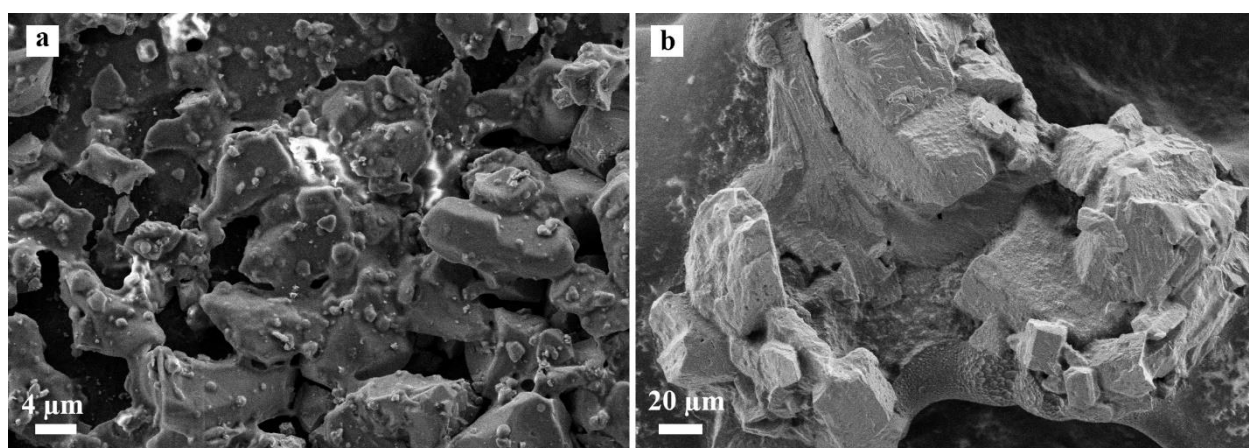


Figure B6. SEM images of working electrode surface (a) before and (b) after 12 h of OER

Estimation of Effective Electrode Surface Area

The electrochemical double-layer capacitance (C_{dl}) for virgin VB_2 and Co-substituted VB_2 catalysts was determined by cyclic voltammograms (CV) under a non-Faradaic region. This range is normally a 0.1 V potential window located on the open-circuit potential (OCP) of the system. Thus, CV experiments were conducted at varying scan rates (0.05, 0.1, 0.2, 0.4, and 0.8 $V s^{-1}$) across a potential region of 0-0.1 V vs. RHE. This region was selected based on the OCP of electrodes (0.05 V) and current against different scan rates was plotted at 0.05 V vs. RHE. Concerning this, the double-layer capacitance was estimated according to:

$$i_c = \nu C_{dl} \quad (\text{Equation B2})$$

where, i_c , ν , and C_{dl} stand for double layer charging current, scan rate, and double-layer capacitance, individually. Finally, the electrochemically active surface area (ECSA) was calculated by the following equation:

$$ECSA = C_{dl}/C_s \quad (\text{Equation B3})$$

where C_s is the specific capacitance of the sample. The typically reported value for C_s in the literature[311] is 0.040 $mF cm^{-2}$ under 1 M KOH solution.

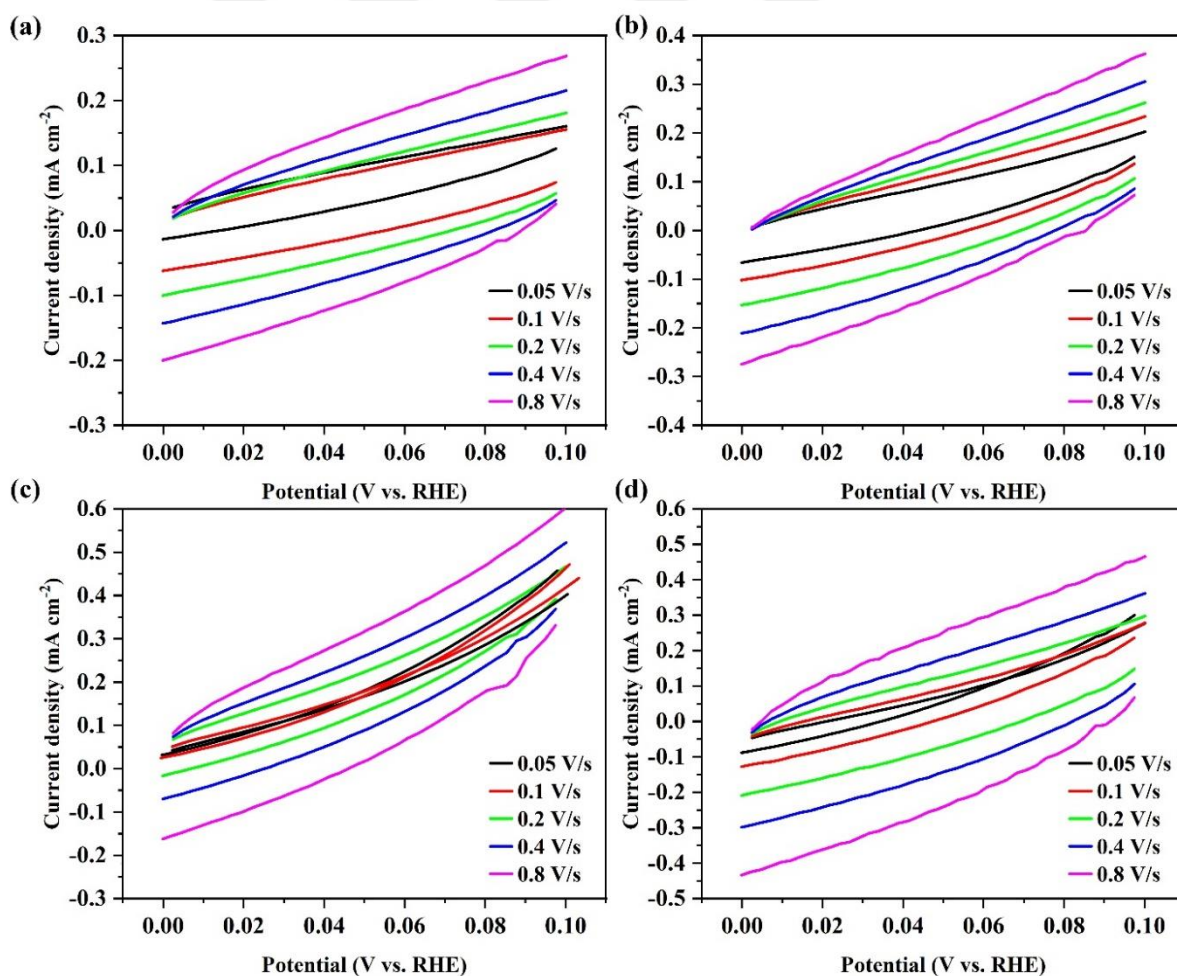


Figure B7. Cyclic voltammograms of (a) VB_2 (b) $V_{0.95}Co_{0.05}B_2$ (c) $V_{0.9}Co_{0.1}B_2$ (d) $V_{0.8}Co_{0.2}B_2$ at various scan rates

Table B 2. Surface composition from XPS spectra (in atomic percent) of VB_2 and $\text{V}_{1-x}\text{Co}_x\text{B}_2$ powders.

Sample	B 1s	V 2p	O 1s	Co 2p
VB_2	5.38	12.2	53.06	-
$\text{V}_{0.95}\text{Co}_{0.05}\text{B}_2$	23.96	7.2	38.62	1.23
$\text{V}_{0.9}\text{Co}_{0.1}\text{B}_2$	21.06	6.43	33.33	1.48
$\text{V}_{0.8}\text{Co}_{0.2}\text{B}_2$	23.58	5.23	32.21	1.95

References

1. A. T. Swesi, J. Masud, M. J. E. Nath and E. Science, *Energy & Environmental Science*, 2016, **9**, 1771-1782.
2. C. C. McCrory, S. Jung, J. C. Peters and T. F. J. J. o. t. A. C. S. Jaramillo, *Journal of the American Chemical Society*, 2013, **135**, 16977-16987.

Appendix C



Figure C1. The coupling mechanism of $\text{Ni}(\text{OH})_2$ as the dominant phase of NCF with Ni-BDC ligand.

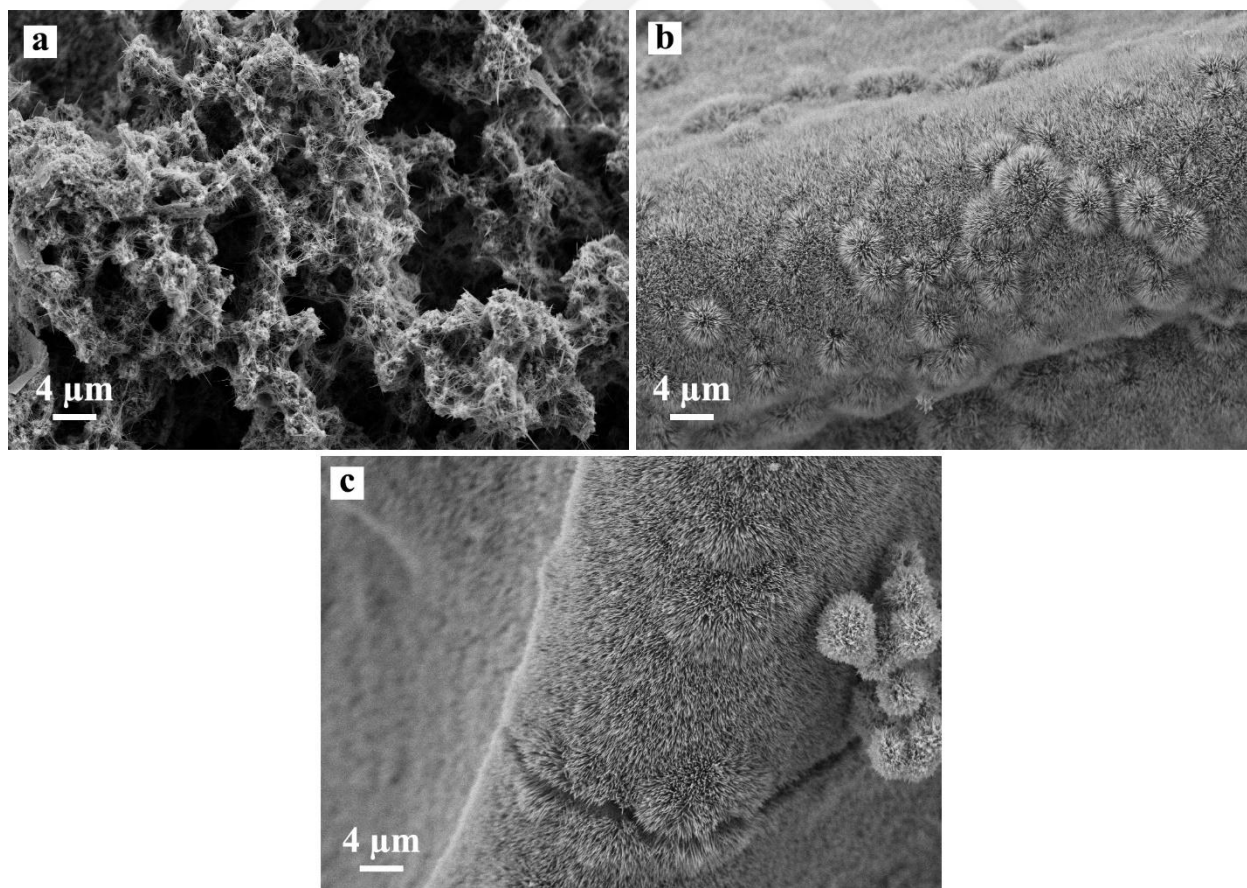


Figure C2. SEM micrographs of a) NCF@NF, b) NCC@NF, and c) NCZ@NF grown on NF backbone with low magnifications.

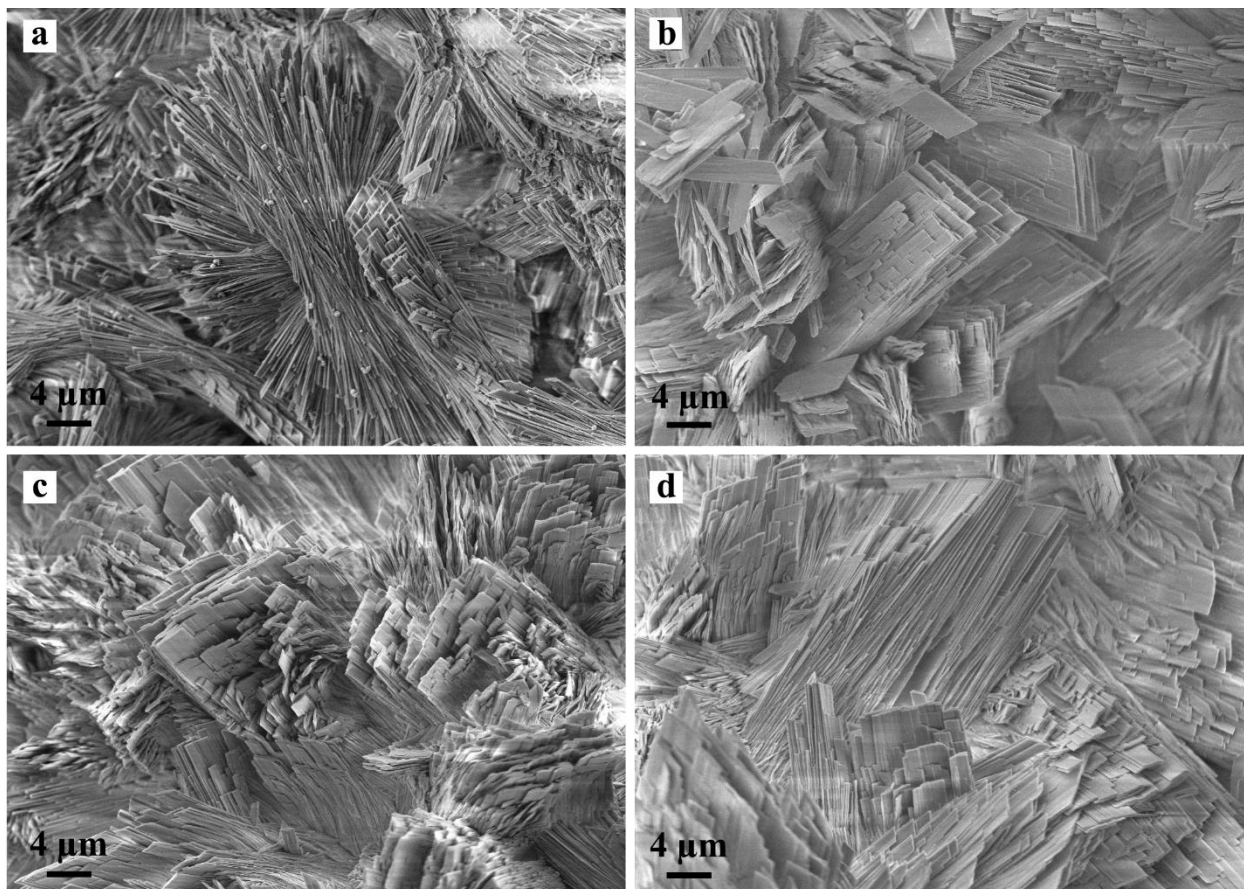


Figure C3. Top-view SEM images of a) Ni-BDC@NF, b) NCF/Ni-BDC@NF, c) NCC/Ni-BDC@NF, and d) NCZ/Ni-BDC@NF.

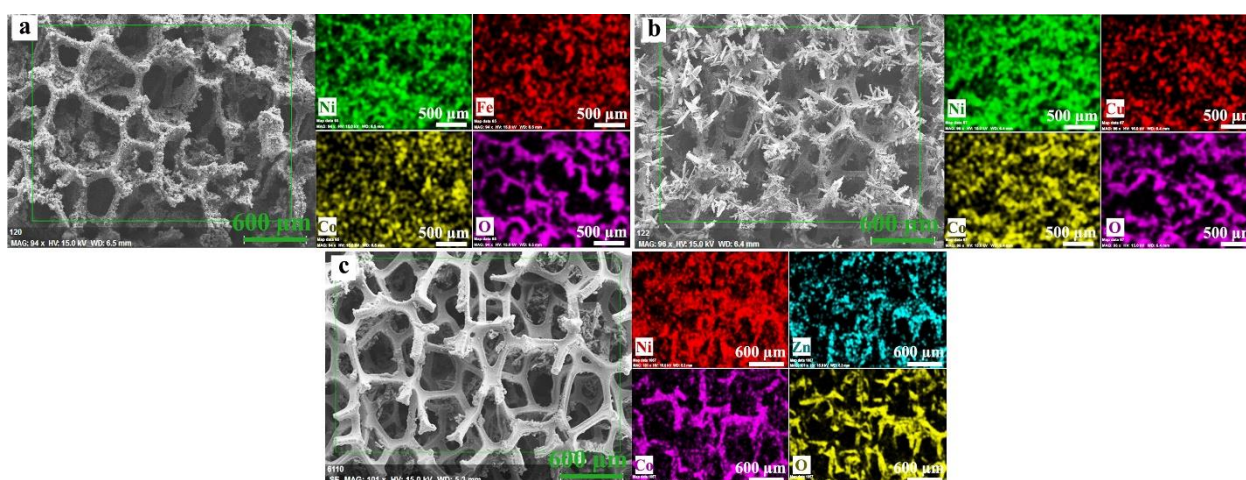


Figure C4. SEM/EDS elemental mappings of a) NCF@NF, b) NCC@NF, and c) NCZ@NF; a very large area selected to observe the distribution of elements throughout the NF.

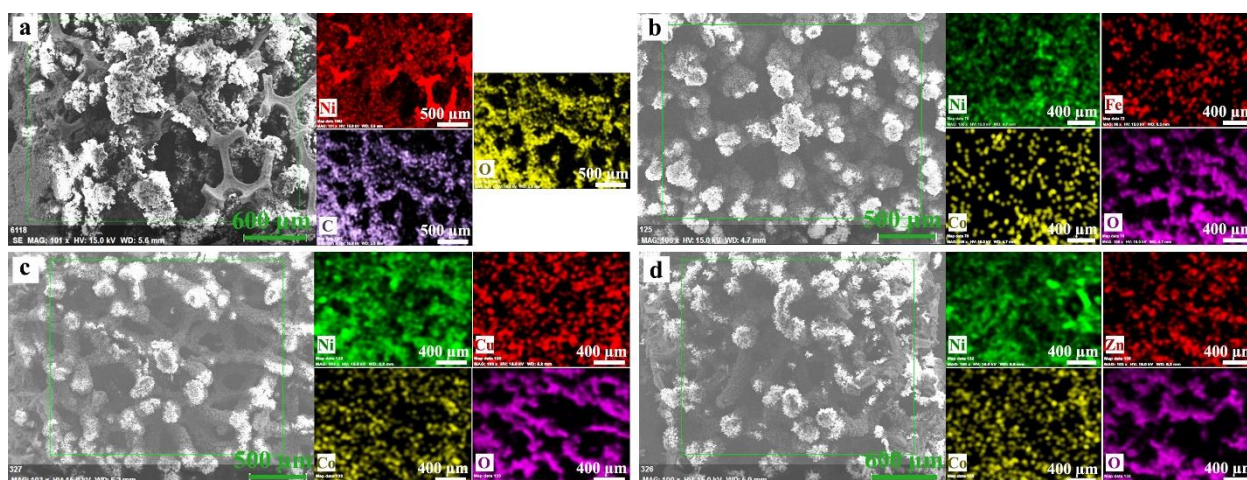


Figure C5. SEM/EDS elemental mappings of a) Ni-BDC@NF, b) NCF/Ni-BDC@NF, c) NCC/Ni-BDC@NF, and d) NCZ/Ni-BDC@NF; a very large area selected to observe the distribution of elements throughout the NF.

Table C 1. The quantitative results of XRF analysis of ternary mixed oxides.

Sample	Elements	Line 1	Concentration (wt%)	Line 2	Concentration (wt%)
NCF	Ni	Ni K α 1	43.34	Ni K β 1	42.18
	Co	Co K α 1	28.33	Co K β 1	27.18
	Fe	Fe K α 1	28.33	Fe K β 1	30.64
NCC	Ni	Ni K α 1	46.55	Ni K β 1	42.34
	Co	Co K α 1	34.65	Co K β 1	38.46
	Cu	Cu K α 1	18.80	Cu K β 1	19.20
NCZ	Ni	Ni K α 1	40.70	Ni K β 1	38.86
	Co	Co K α 1	24.30	Co K β 1	25.83
	Zn	Zn K α 1	35.00	Zn K β 1	35.31

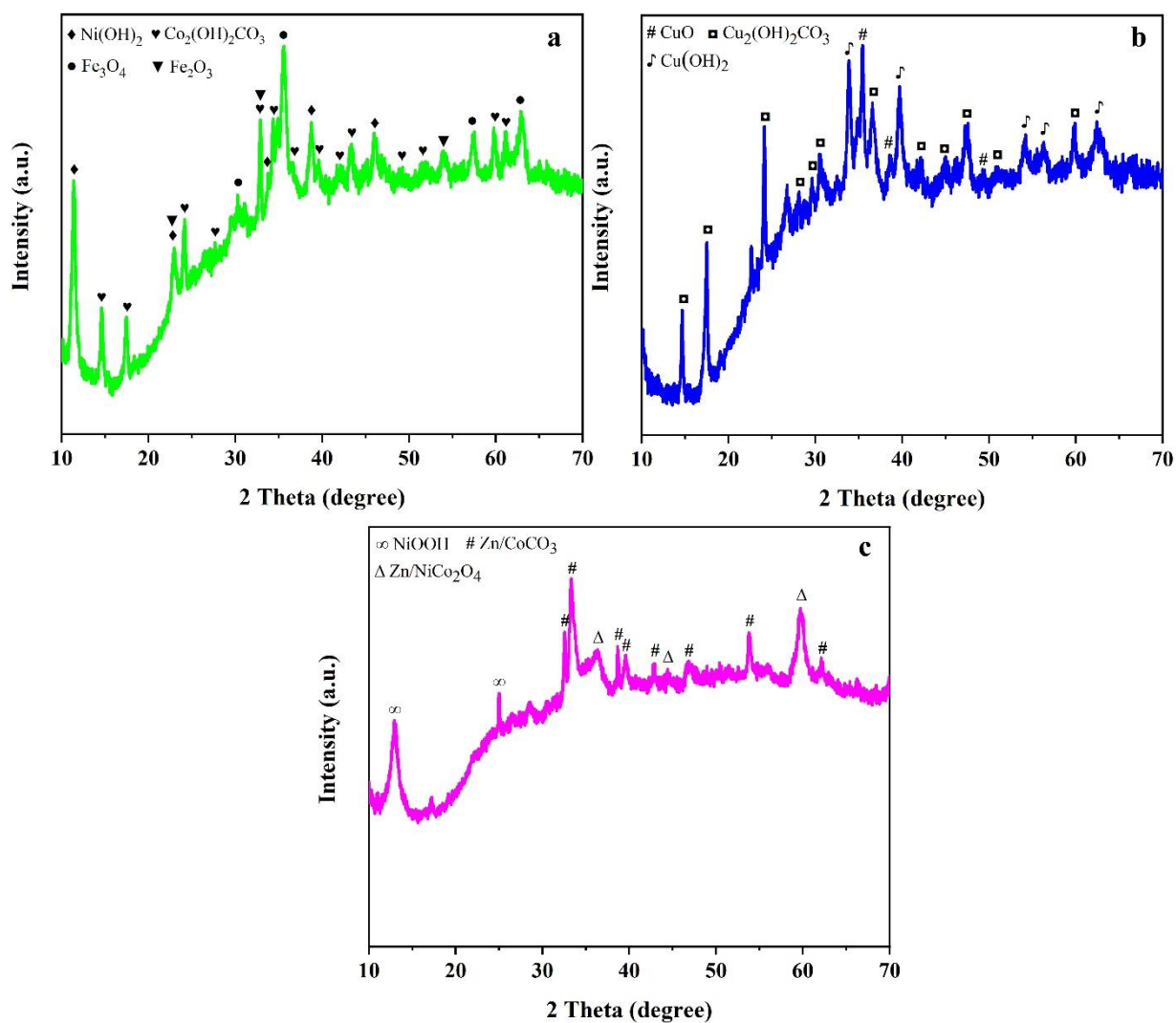


Figure C6. XRD patterns of various ternary oxides, NCM (M = F, C, and Z) stripped off from NF.

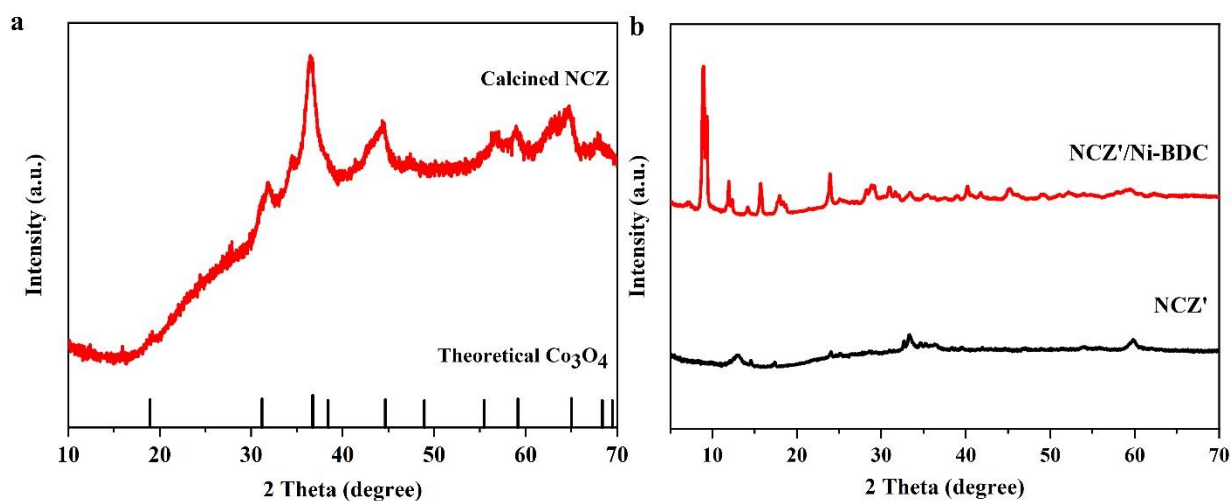


Figure C7. XRD patterns of a) Calcined NCZ catalyst sample and b) Ternary oxide NCZ' and its corresponding nanocomposite NCZ'/Ni-BDC stripped off from NF.

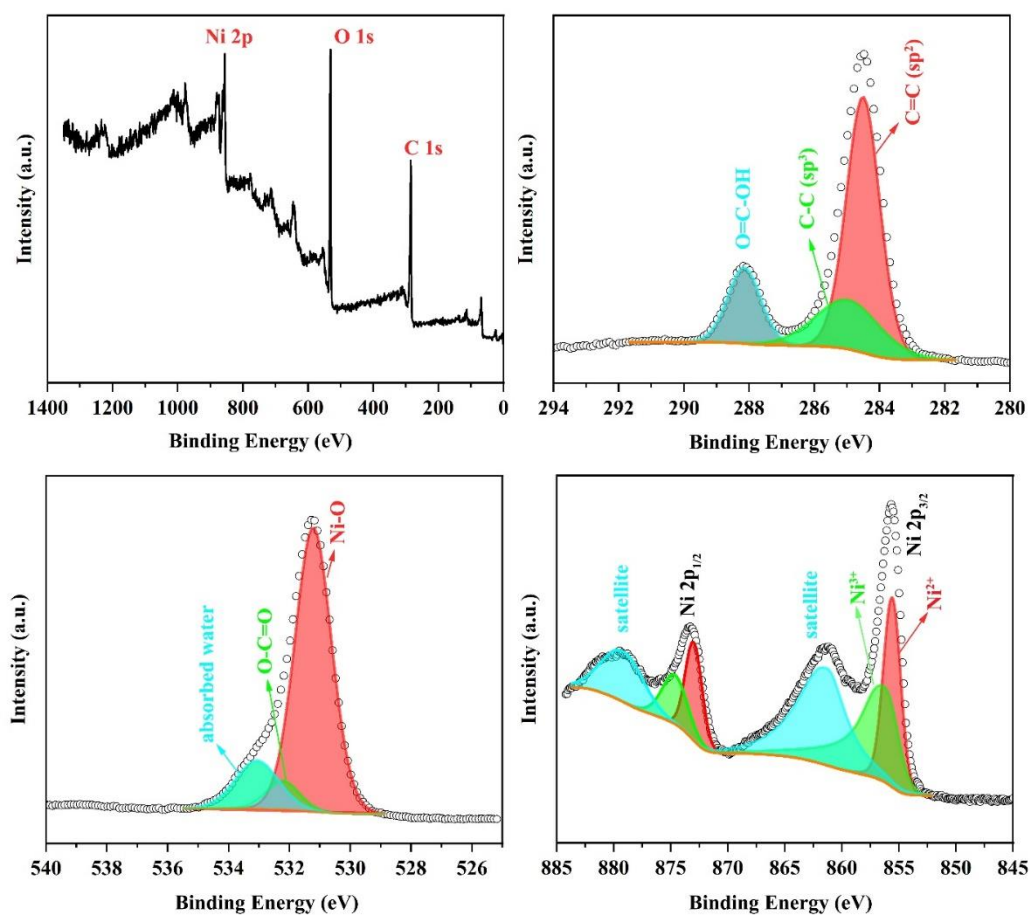


Figure C8. XPS survey, C 1s, O 1s, and Ni 2p spectra for Ni-BDC stripped off from NF.

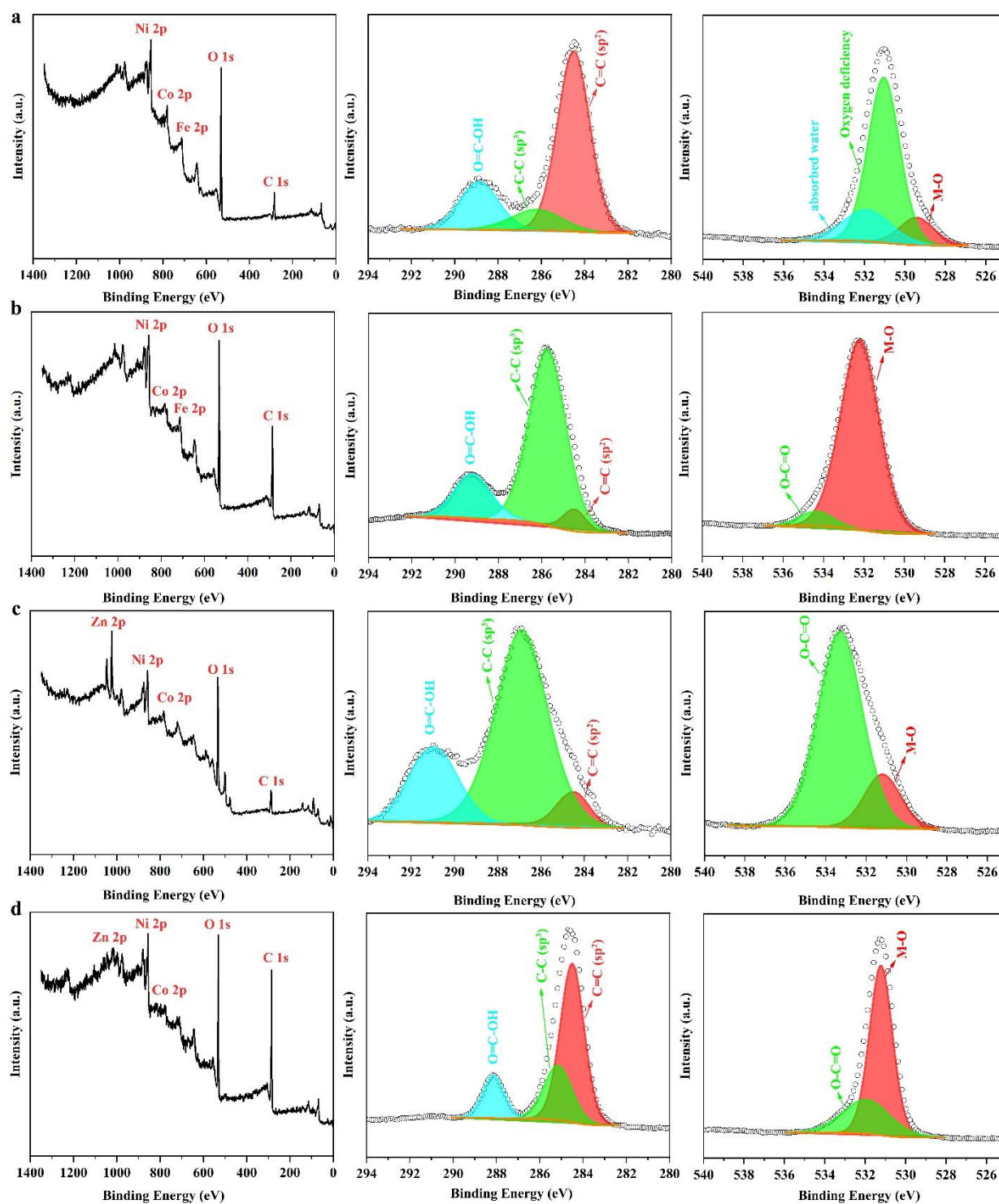


Figure C9. XPS survey, C 1s, and O 1s spectra for a) NCF, b) NCF/Ni-BDC, c) NCZ, and d) NCZ/Ni-BDC stripped off from NF.

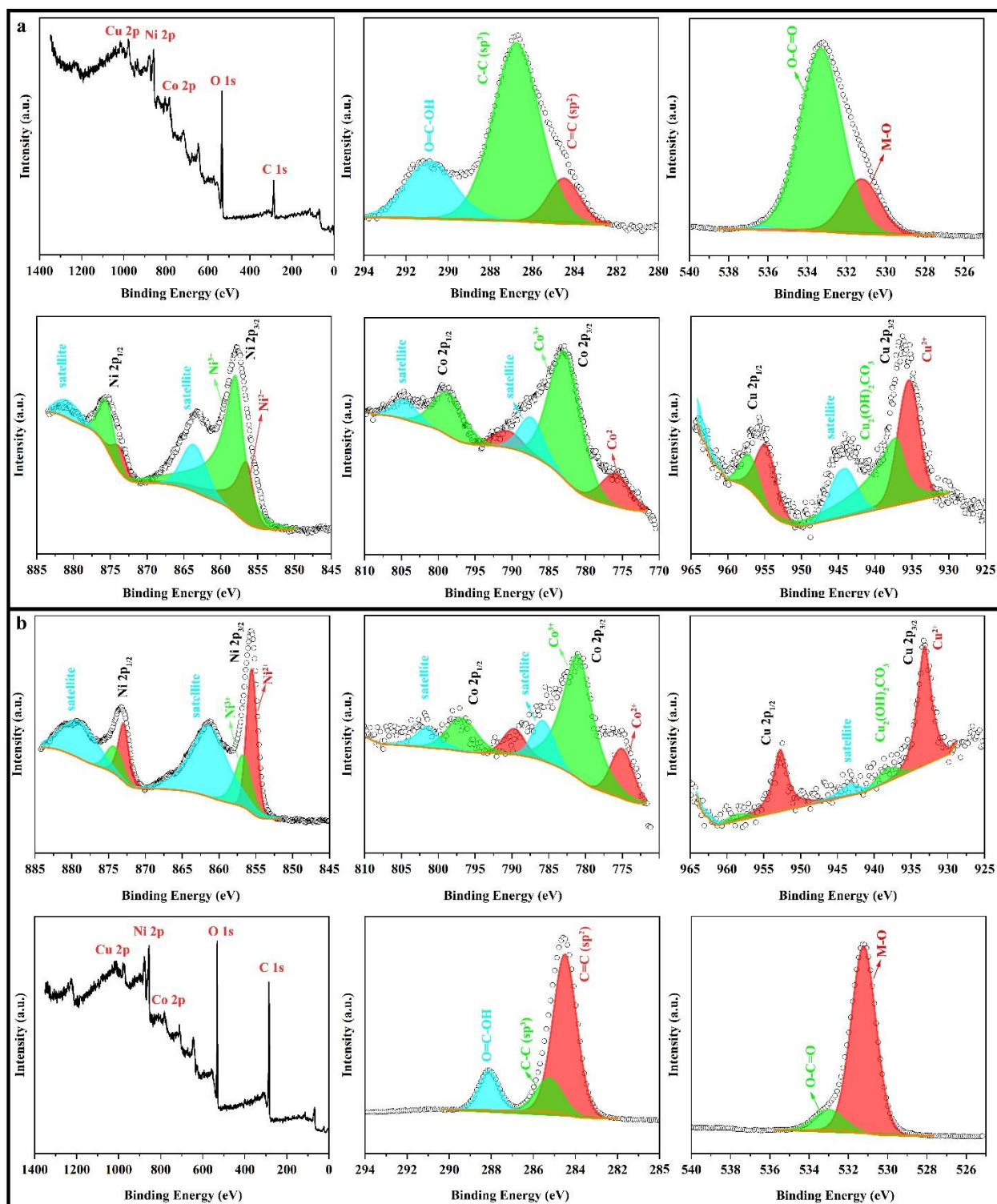


Figure C10. a) XPS survey, C 1s, O 1s, Ni 2p, Co 2p, and Cu 2p spectra for NCC and b) XPS Ni 2p, Co 2p, Cu 2p, survey, C 1s, and O 1s spectra for NCC/Ni-BDC stripped off from NF.

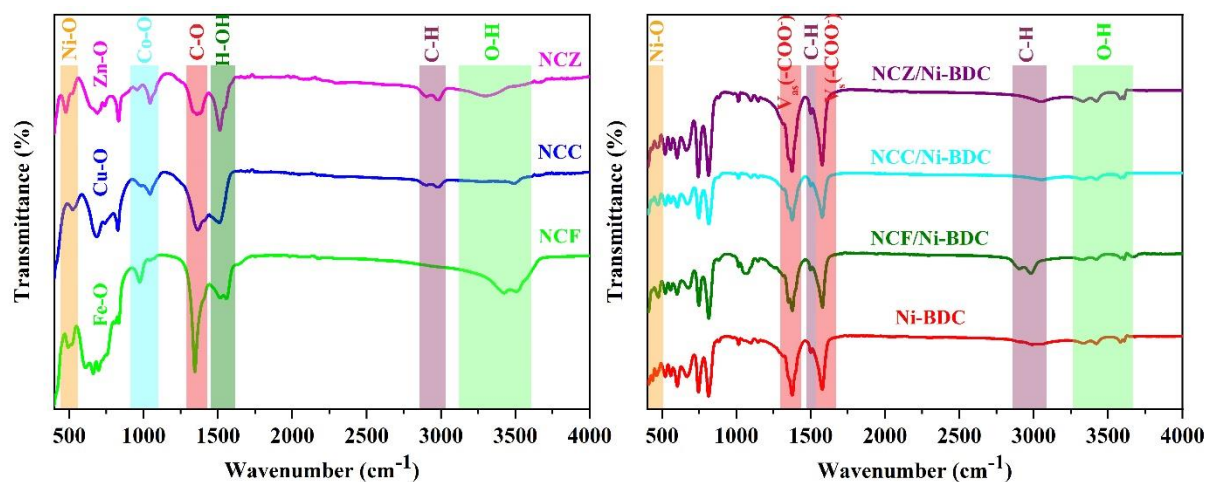


Figure C11. FT-IR spectra of ternary oxides and their corresponding nanocomposites stripped off from NF.

Table C 2. The OER, HER, and overall water splitting performances of recent reports on MOF-derivative catalysts in terms of overpotential at 10 mA cm⁻² (η^{10}) and 50 mA cm⁻² (η^{50}) current densities.

Sample	η_{OER} (mV)	η_{HER} (mV)	Cell voltage (V)	Catalyst loading
Ni-BDC/NF	$\eta^{10} = 436$	-	-	12.8 mg cm ⁻²
Ni ₃ S ₄ /NF	$\eta^{10} = 266$	-	-	
Ni ₃ S ₄ /NF Ni ₃ S ₄ /NF [15]	-	-	1.638 @ 10 mA cm ⁻²	
NF@Ni/C-600	$\eta^{10} = 265$	$\eta^{10} = 37$	-	7.0 mg cm ⁻²
	$\eta^{50} = 353$	$\eta^{50} = 124$	-	
NF@Ni/C-600 NF@Ni/C-600 [168]	-	-	1.60 @ 10 mA cm ⁻²	
NiFe-LDH [312]	$\eta^{50} = 270$	-	-	-
NF@Fe ₂ -Ni ₂ P/C	$\eta^{10} = 205$	-	-	3.9 ± 0.3 mg cm ⁻²
NF@Fe ₂ -Ni/C	-	$\eta^{10} = 33$	-	
NF@Fe ₂ -Ni ₂ P/C NF@Fe ₂ -Ni ₂ P/C [227]	-	-	1.57 @ 100 mA cm ⁻²	
Fe-Ni@NC-CNT [16]	$\eta^{10} = 274$	$\eta^{10} = 202$	-	1.0 mg cm ⁻²
Ni@NC-800	$\eta^{10} = 280$	$\eta^{10} = 205$	-	0.8 mg cm ⁻²
	-	-		

Ni@NC-800NF Ni@NC-800NF [19]			1.60 @ 10 mA cm ⁻²	
NiFe-MOF NiFe-MOF NiFe-MOF [213]	$\eta^{10} = 240$ -	$\eta^{10} = 134$ -	- 1.55 @ 10 mA cm ⁻²	-
NFN-MOF/NF NFN-MOF/NF NFN-MOF/NF [80]	$\eta^{10} = 240$ -	$\eta^{10} = 87$ -	- 1.56 @ 10 mA cm ⁻²	0.6 mg cm ⁻²
(Ni _x Fe _{1-x}) ₂ P (Ni _x Fe _{1-x}) ₂ P (1.0 mM) Ni ₂ P [226]	$\eta^{10} = 166$ -	$\eta^{10} = 125$ -	- 1.56 @ 10 mA cm ⁻²	1.0 mg cm ⁻²
Ru-doped NiFeP/NF Ru-NiFeP/NF Ru-NiFeP/NF [211]	$\eta^{10} = 179$ -	$\eta^{10} = 56$ -	- 1.47 @ 10 mA cm ⁻²	10 mg cm ⁻²
Ni ₃ S ₄ Ni ₃ S ₄ Pt/C [188]	$\eta^{10} = 257$ $\eta^{50} = 300$ -	- - -	- - 1.51 @ 10 mA cm ⁻²	11 mg cm ⁻²
NiRu _{0.13} -BDC [185]	-	$\eta^{10} = 36$	-	2.5 mg cm ⁻²
Zn-Ni-Co-S/NF Zn-Ni-Co-P/NF Zn-Ni-Co-S/NF Zn-Ni-Co-P/NF [171]	$\eta^{50} = 190$ - -	- $\eta^{10} = 94$ -	- - 1.52 @ 10 mA cm ⁻²	-
Co-Fe oxide Co-Fe oxide Co-Fe oxide [212]	$\eta^{20} = 369$ $\eta^{100} = 406$ -	$\eta^{10} = 220$ $\eta^{100} = 290$ -	- - 1.92 @ 10 mA cm ⁻²	6.0 mg cm ⁻²
Ni-BDC Ni(OH) ₂ Ni-BDC/Ni(OH) ₂ [179]	$\eta^{10} = 358$ $\eta^{10} = 395$ $\eta^{10} = 320$	- - -	- - -	-
NiCo LDH@ZIF-67-V _O /NF [313]	$\eta^{10} = 290$	-	-	-

Table C 3. The OER and HER performances of fabricated catalysts in this work in terms of overpotential at 10 mA cm⁻² (η^{10}) and 50 mA cm⁻² (η^{50}) current densities, charge transfer coefficient (α) for OER, and exchange current density (j^0) for HER.

Sample	η^{10}_{OER} (mV)	η^{50}_{OER} (mV)	α	η^{10}_{HER} (mV)	η^{50}_{HER} (mV)	j^0 (mA cm ⁻²)
NF	380	-	0.23	314	435	0.017
RuO ₂ @NF	260	430	0.54	-	-	-
Pt/C@NF	-	-	-	61	214	1.08
Ni-BDC@NF	420	-	0.25	268	442	0.153
NCF@NF	160	350	1.49	231	383	0.316
NCC@NF	400	570	0.31	183	366	0.69
NCZ@NF	230	560	0.86	236	399	0.43
NCF/Ni-BDC@NF	120	450	1.68	215	373	0.382
NCC/Ni-BDC@NF	310	550	0.32	215	385	0.62
NCZ/Ni-BDC@NF	190	520	0.98	170	351	0.78

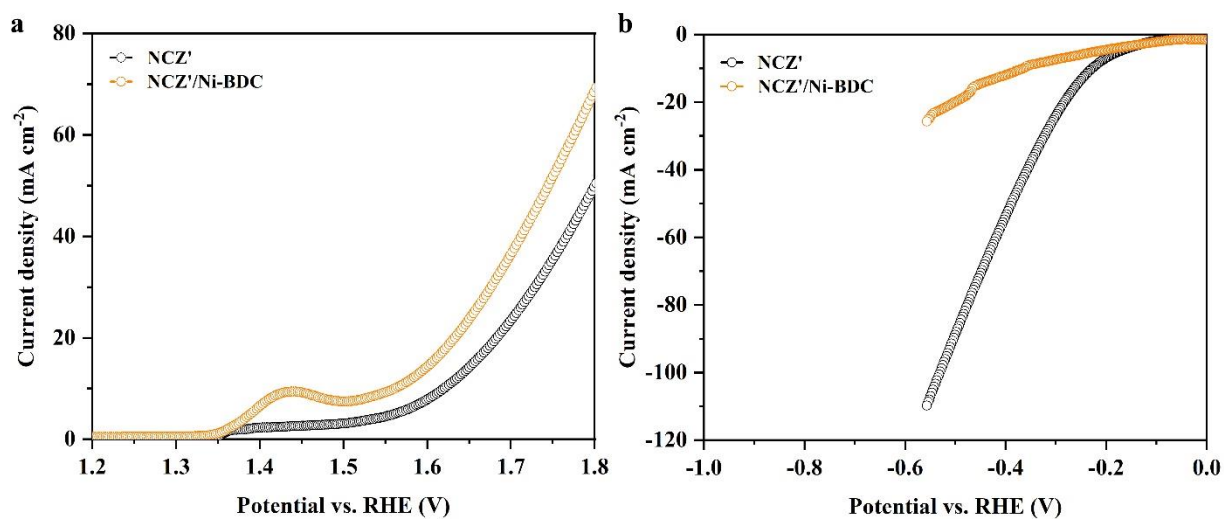


Figure C12. Electrochemical performance of NCZ' and NCZ'/Ni-BDC, a) OER and b) HER.

Table C 4. Estimated values obtained from the EIS simulations by the ZView software.

Sample	R_e (Ω)	CPE1 ($mFsp^{-1}$)	R_p (Ω)	CPE2 ($mFsp^{-1}$)	R_{ct} (Ω)
Ni-BDC	2.17	0.0018	51.08	0.0070	494.9
NCF	2.03	0.0017	41.06	0.0089	418.8
NCC	2.26	0.0022	49.5	0.0149	198.9
NCZ	1.76	0.0025	26.17	0.00012	45.7×10^4
NCF/Ni-BDC	2.02	0.0026	29.69	0.0151	116.3
NCC/Ni-BDC	1.96	0.0021	52.96	0.0133	167
NCZ/Ni-BDC	1.97	0.002	17.31	0.0159	126.9
Ni-BDC (-) Ni-BDC (+)	5.17	0.0019	2607	0.00083	37.8×10^9
NCC (-) NCF (+)	6.38	0.0021	3216	0.0012	2818
NCZ/Ni-BDC (-) NCF/Ni-BDC (+)	4.70	0.025	27.9	0.023	423

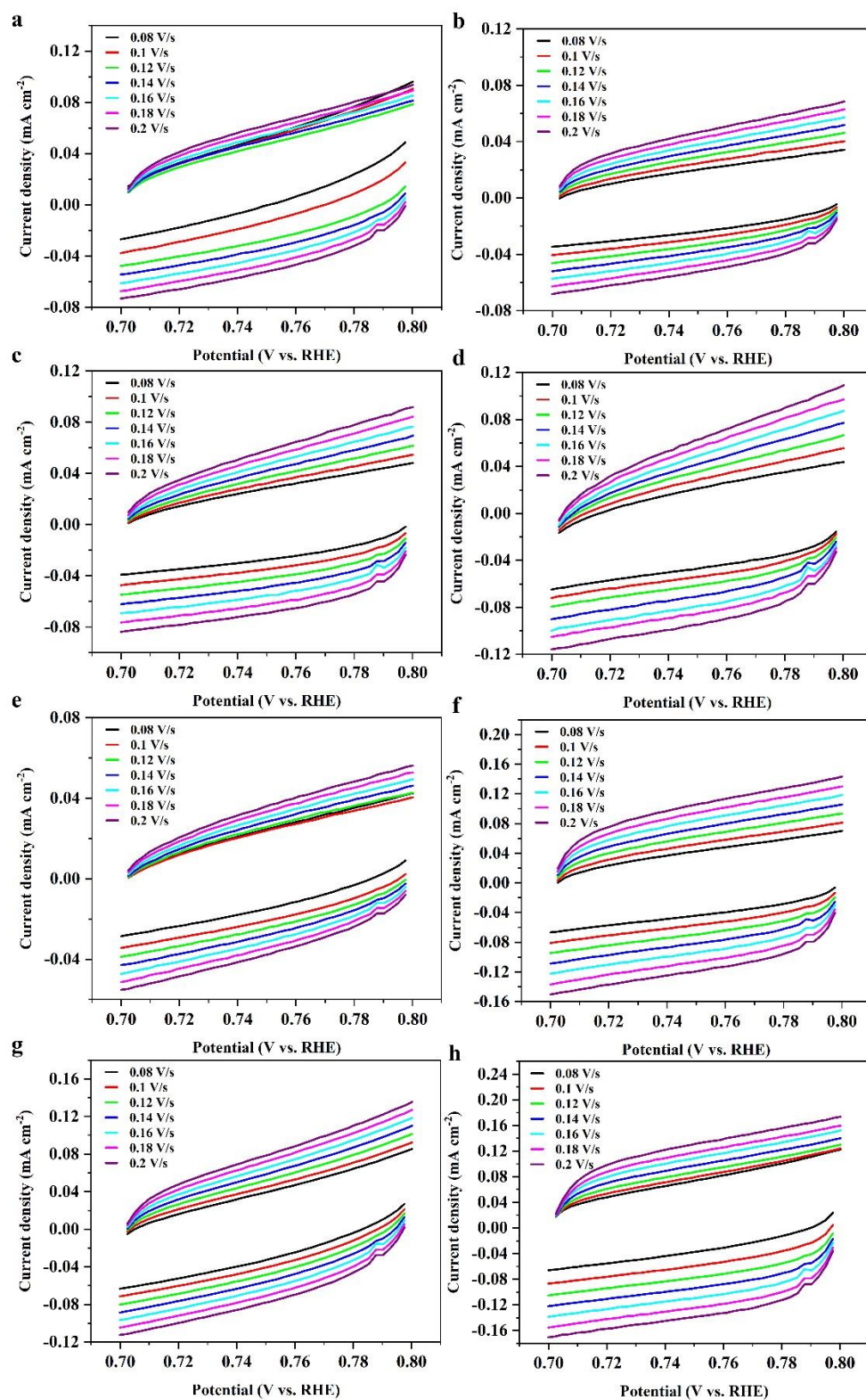


Figure C13. Typical cyclic voltammetry (CV) curves obtained at different scan rates (0.08–0.2 V s⁻¹) within the potential window 0.7–0.8 V vs RHE for a) blank NF, b) Ni-BDC, c) NCF, d) NCC, e) NCZ, f) NCF/Ni-BDC, g) NCC/Ni-BDC, and h) NCZ/Ni-BDC.

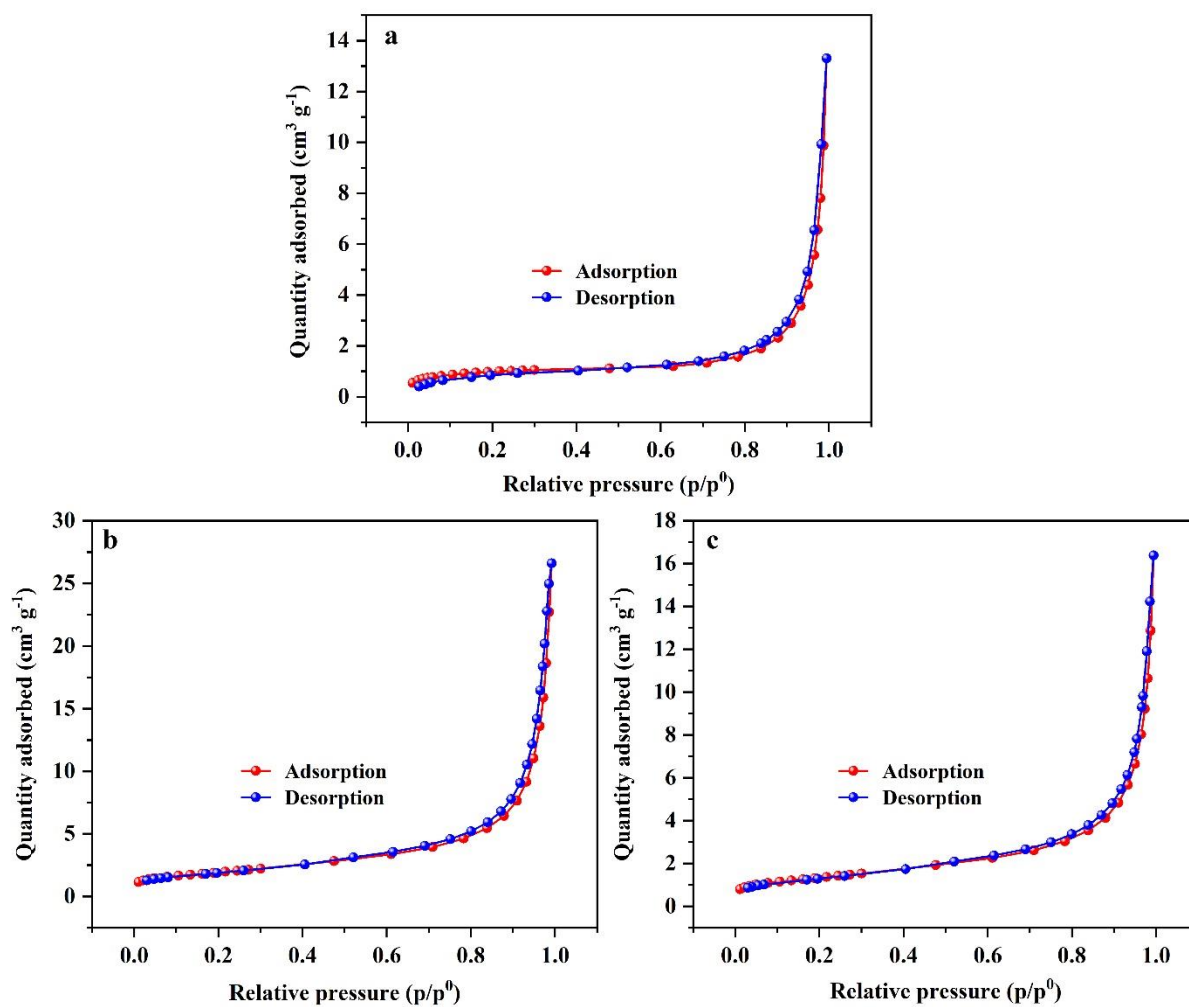


Figure C14. N₂ adsorption-desorption isotherms of a) Ni-BDC, b) NCF/Ni-BDC, and c) NCZ/Ni-BDC.

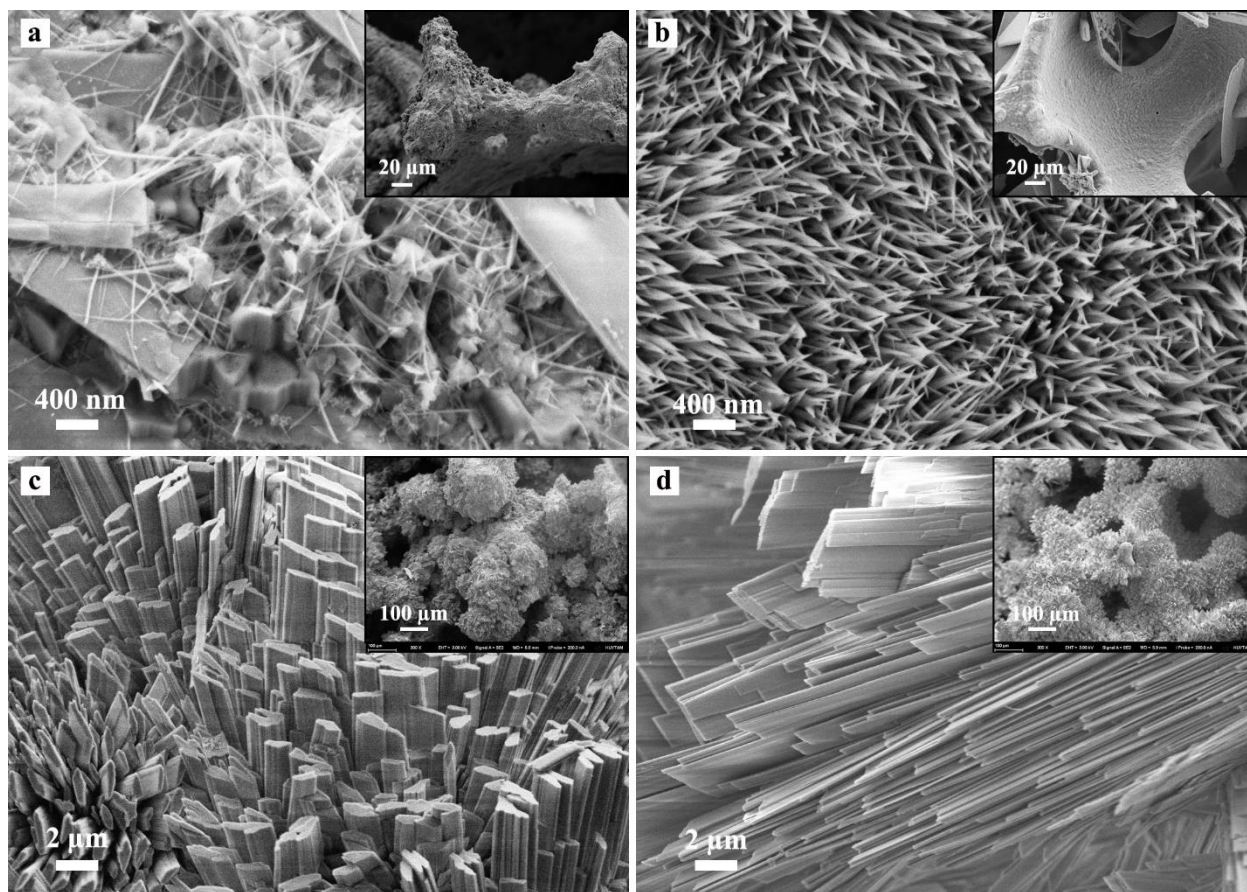


Figure C15. SEM images of a) NCF and c) NCF/Ni-BDC after OER tests, and b) NCC and d) NCZ/Ni-BDC after HER tests.

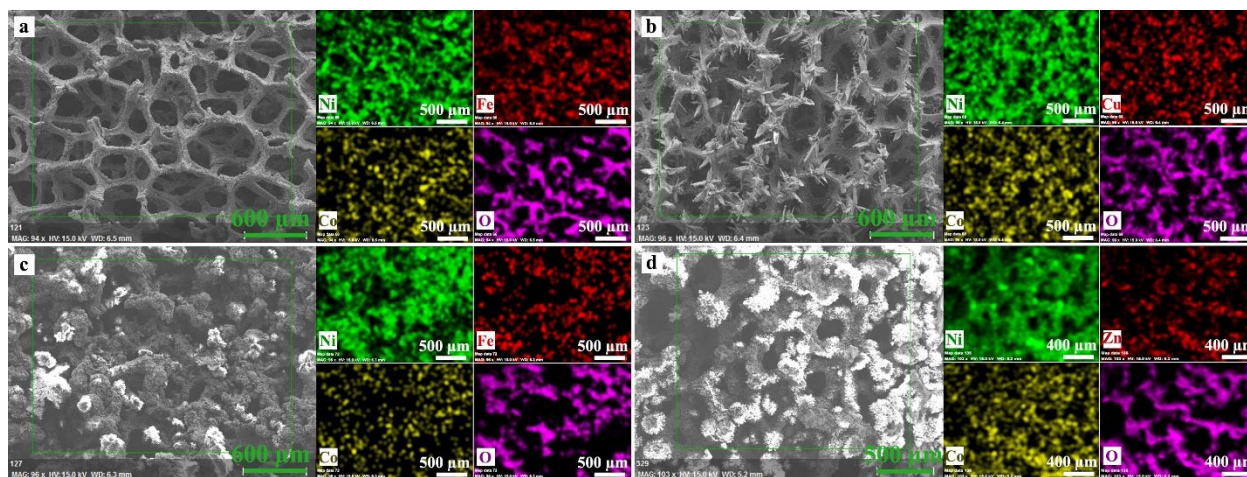


Figure C16. SEM/EDS elemental mappings of a) NCF and c) NCF/Ni-BDC after OER tests, and b) NCC and d) NCZ/Ni-BDC after HER tests.

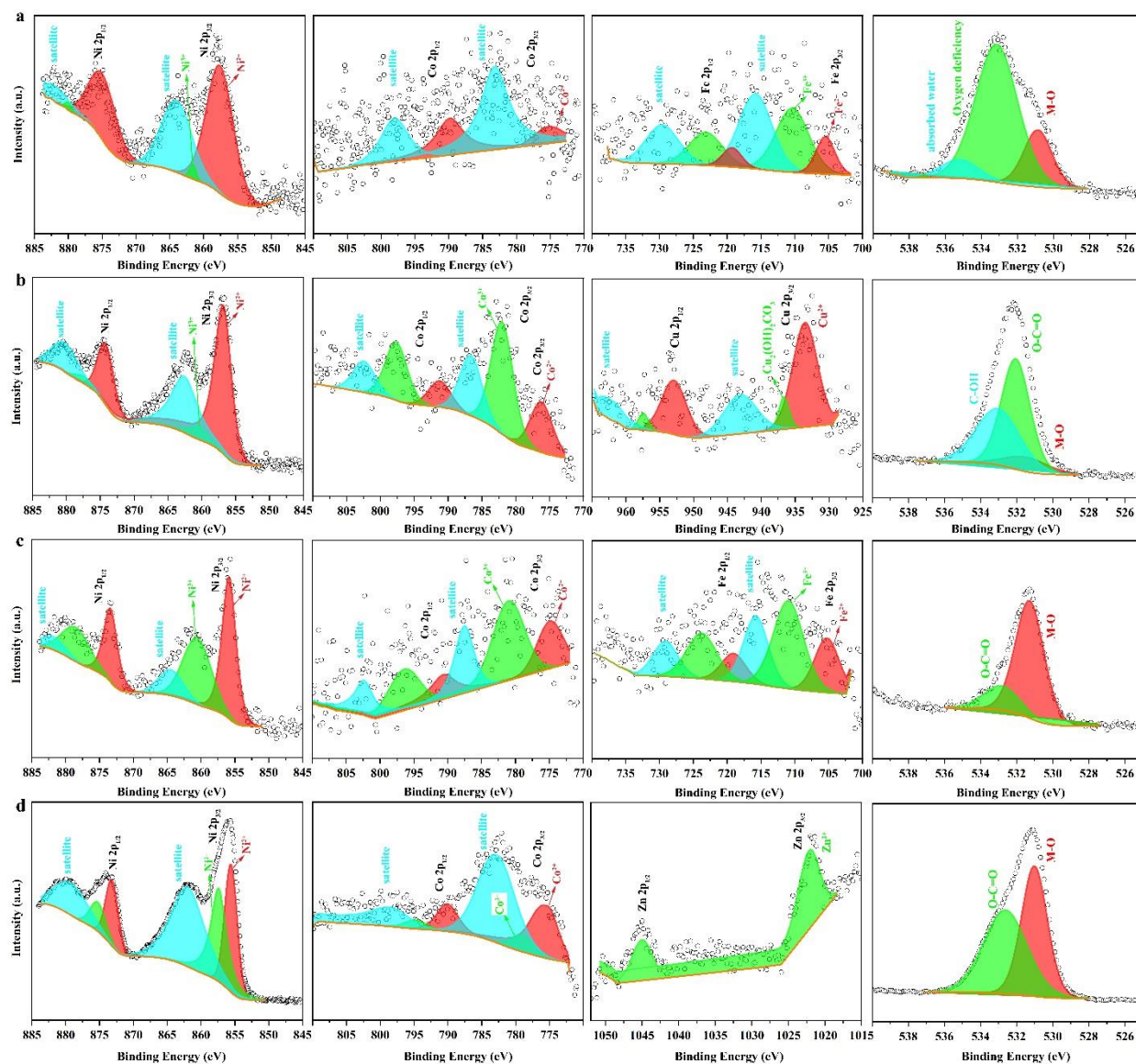


Figure C17. XPS spectra after electrochemical OER and HER measurements. a and c) Ni 2p, Co 2p, Fe 2p, and O 1s for NCF and NCF/Ni-BDC after OER tests and b and d) Ni 2p, Co 2p, Cu 2p, and O 1s for NCC and NCZ/Ni-BDC after HER tests.

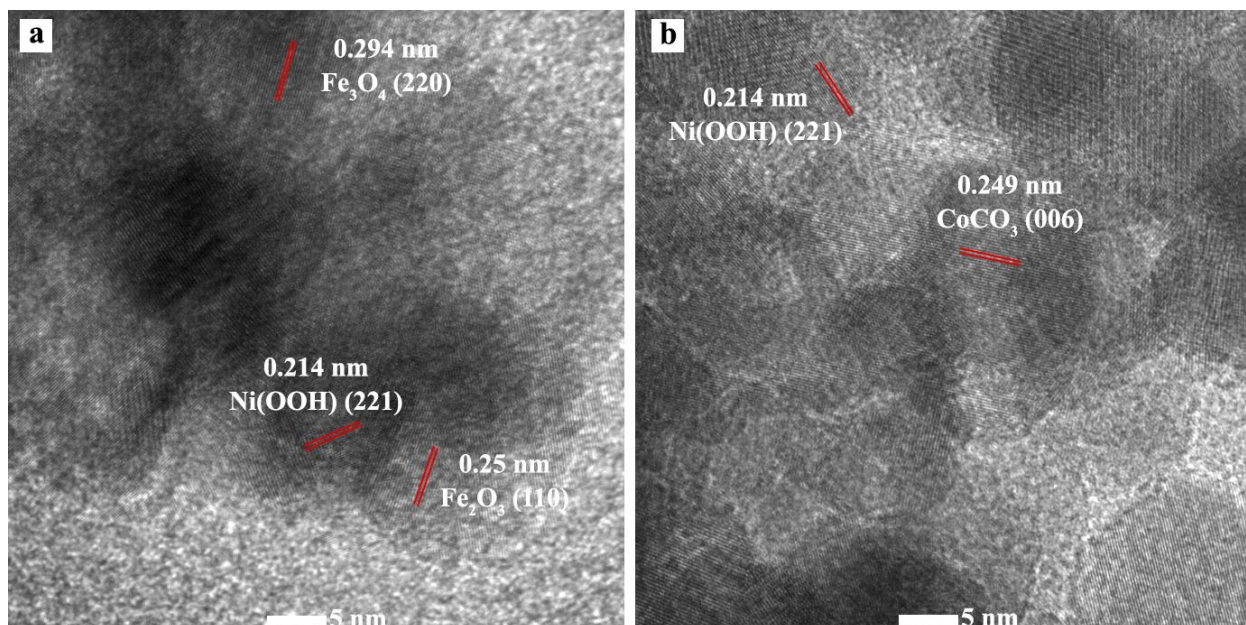


Figure C18. Post-electrolysis HR-TEM photographs. a) NCF/Ni-BDC after the OER durability test and b) NCZ/Ni-BDC after the HER stability test.

Table C 5. . ICP-MS analysis on dissolved elements during OER stability for NCF/Ni-BDC and HER stability for NCZ/Ni-BDC.

Sample	Fe [Conc. (ppb)]	Co [Conc. (ppb)]	Zn [Conc. (ppb)]	Ni [Conc. (ppb)]
NCF/Ni-BDC	9.55	0.14	-	-
NCZ/Ni-BDC	17.81	3.21	40.82	-

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Appendix D

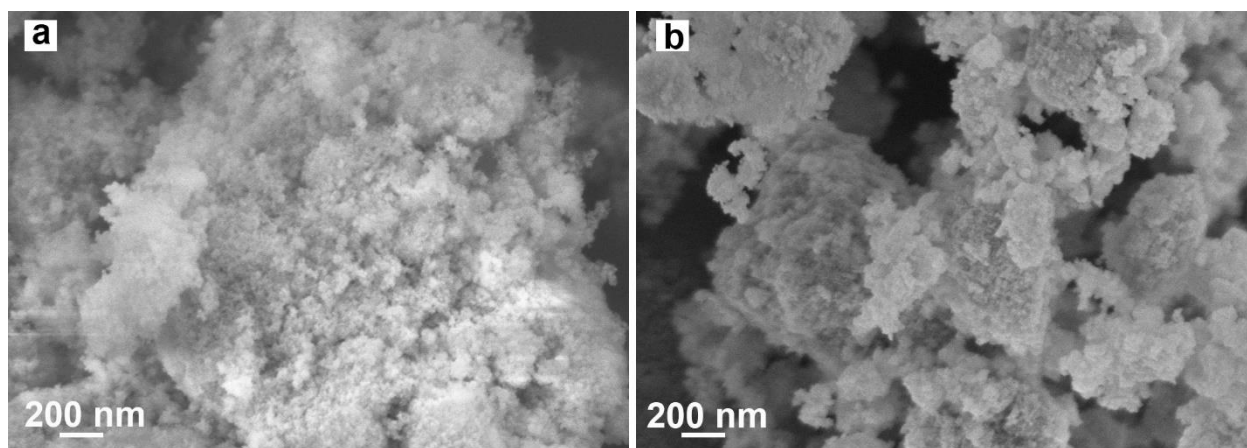
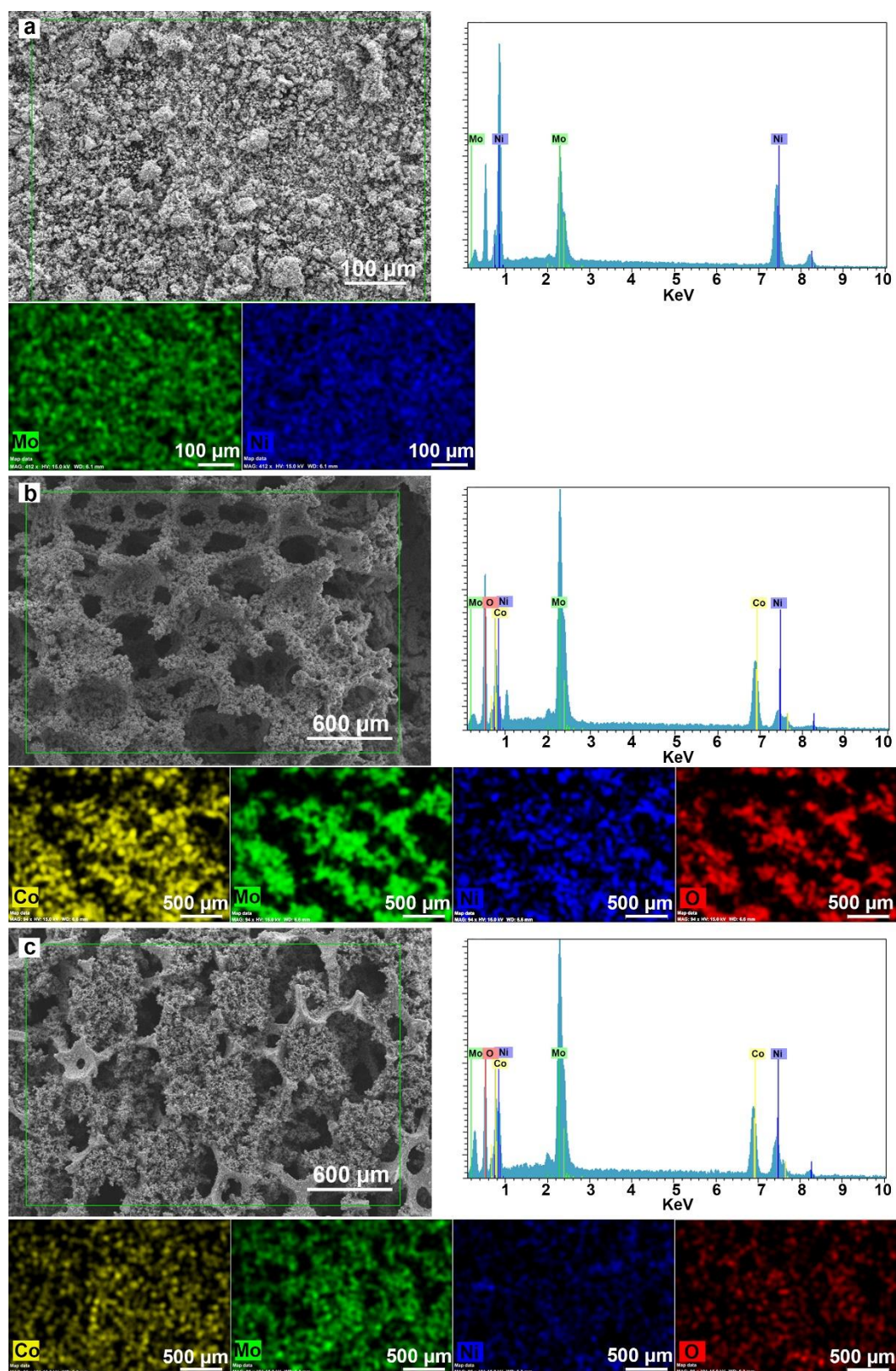


Figure D1. High magnification SEM images on NiMo before and after heat treatment at 550 °C under Ar flow.



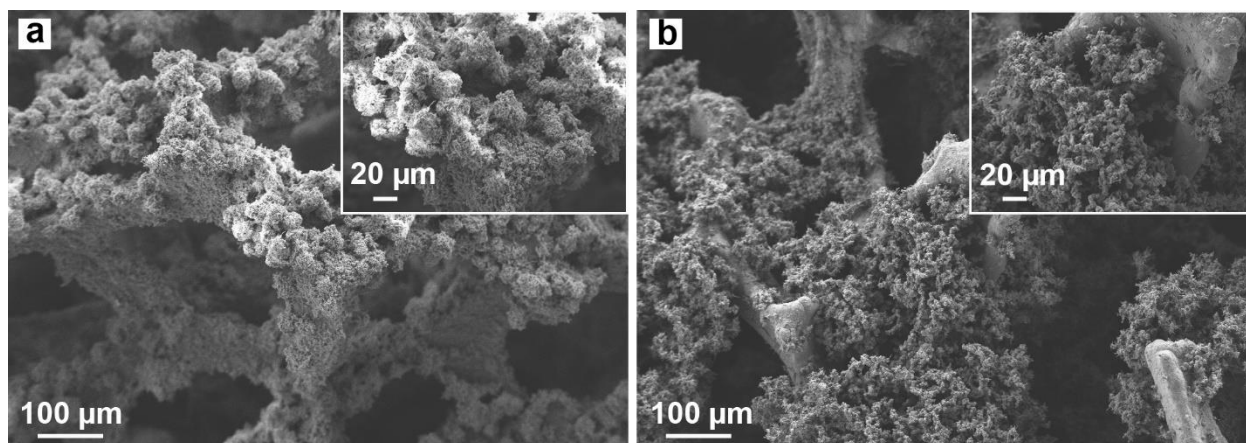


Figure D3. Illustration of uniform growth of catalysts on the backbone of NF substrate, a) CoMoO_4 and b) NiMo/CoMoO_4 .

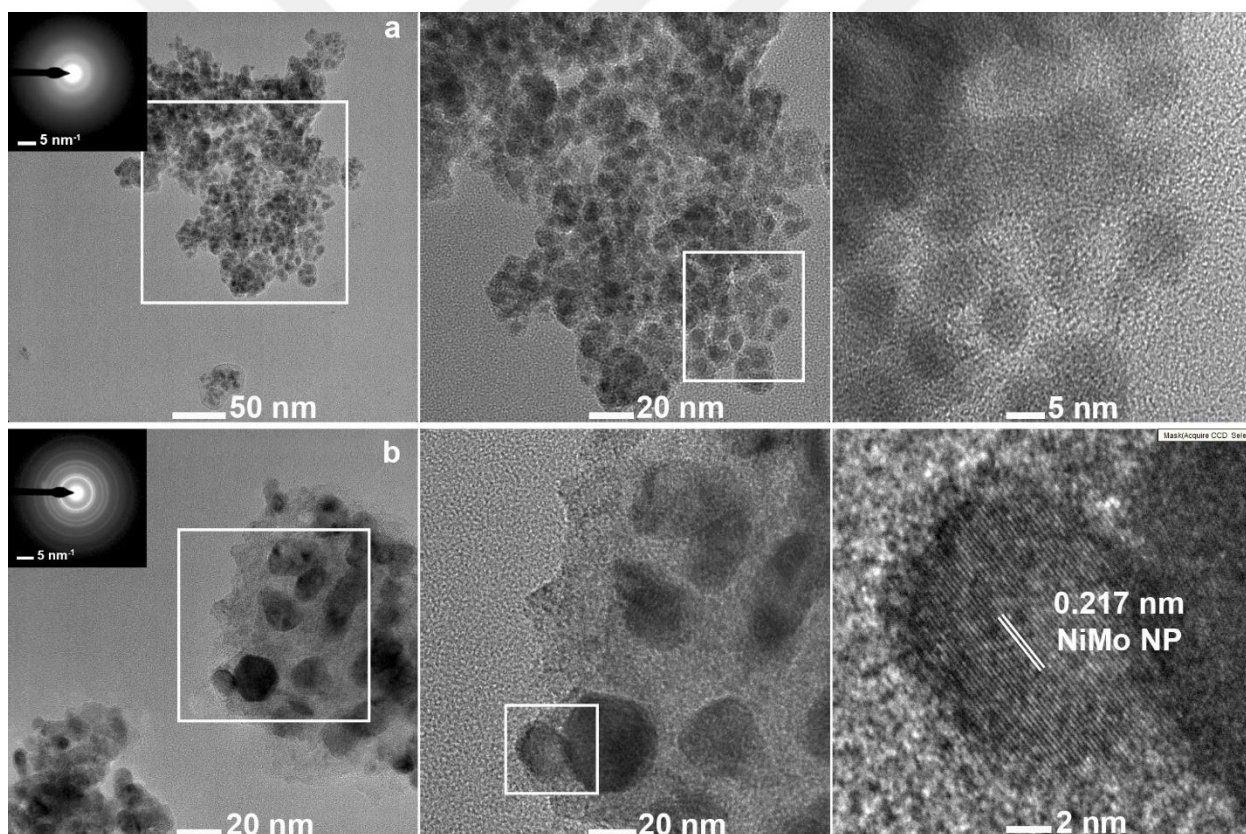


Figure D4. TEM, HR-TEM, and SAED images, a) NiMo NPs before heat treatment and b) NiMo NPs after heat treatment (inset: SAED images).

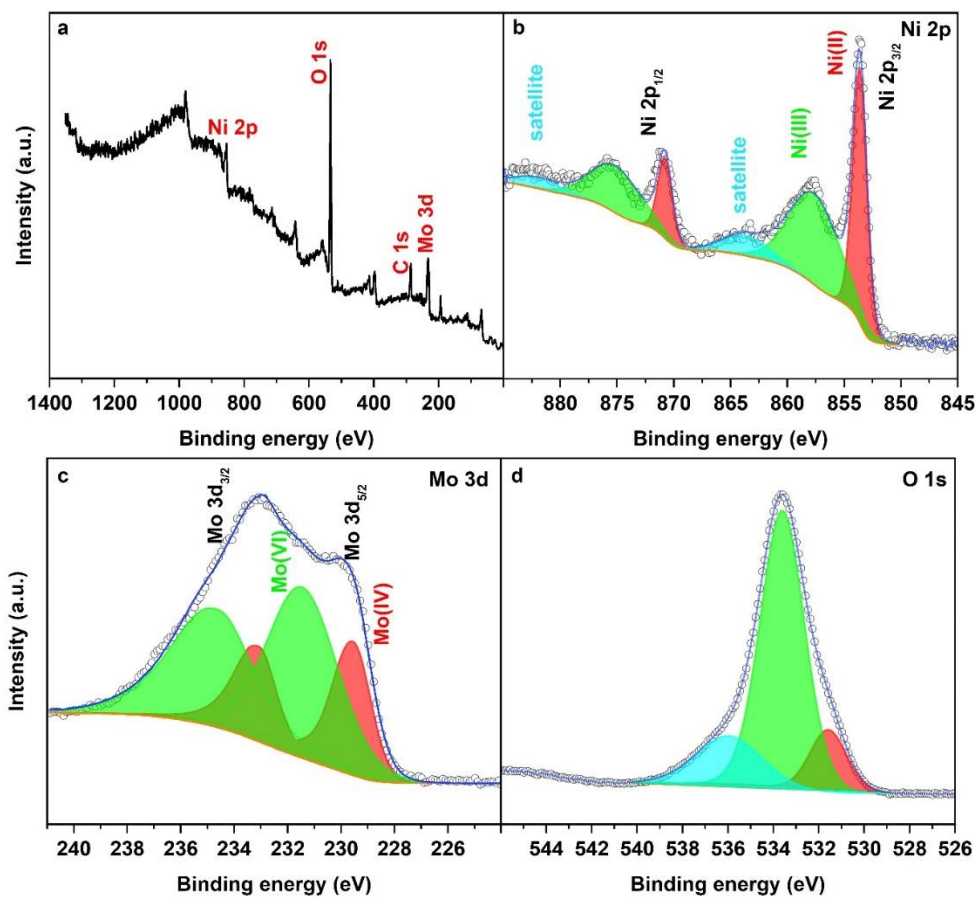


Figure D5. XPS results for NiMo NPs. a) XPS survey, b) Ni 2p, c) Mo 3d, and d) O 1s spectra.

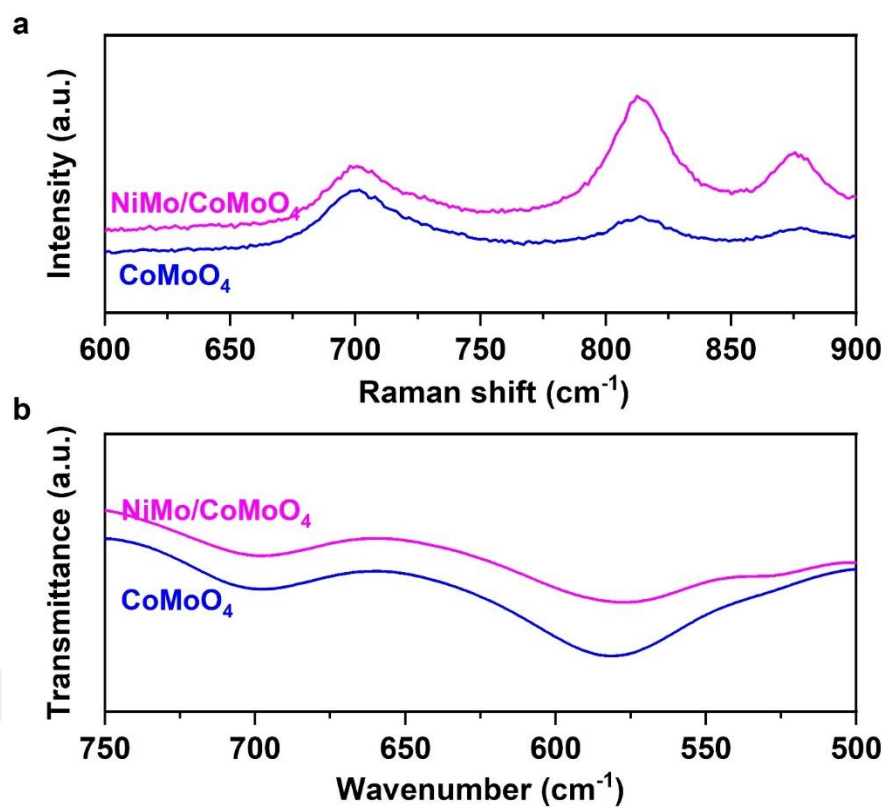


Figure D6. Spectroscopic shifts between pristine CoMoO_4 and NiMo/CoMoO_4 . a) Raman shift and b) FT-IR shift.

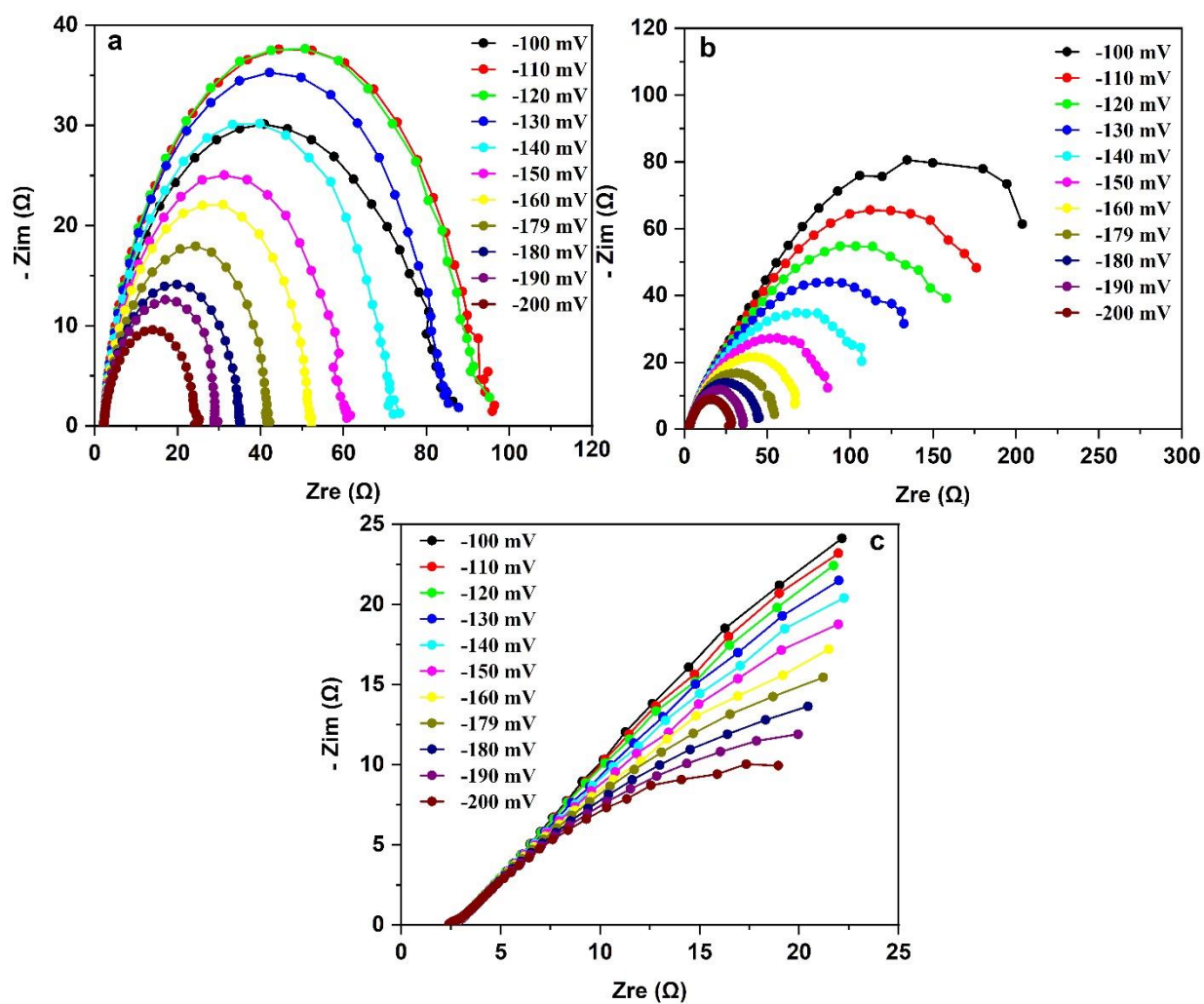


Figure D7. The Nyquist plots obtained through EIS measurements within the reduction potential of 100 – 200 mV vs RHE with an interval of 10 mV. a) NiMo NPs, b) CoMoO₄, and c) NiMo/CoMoO₄.

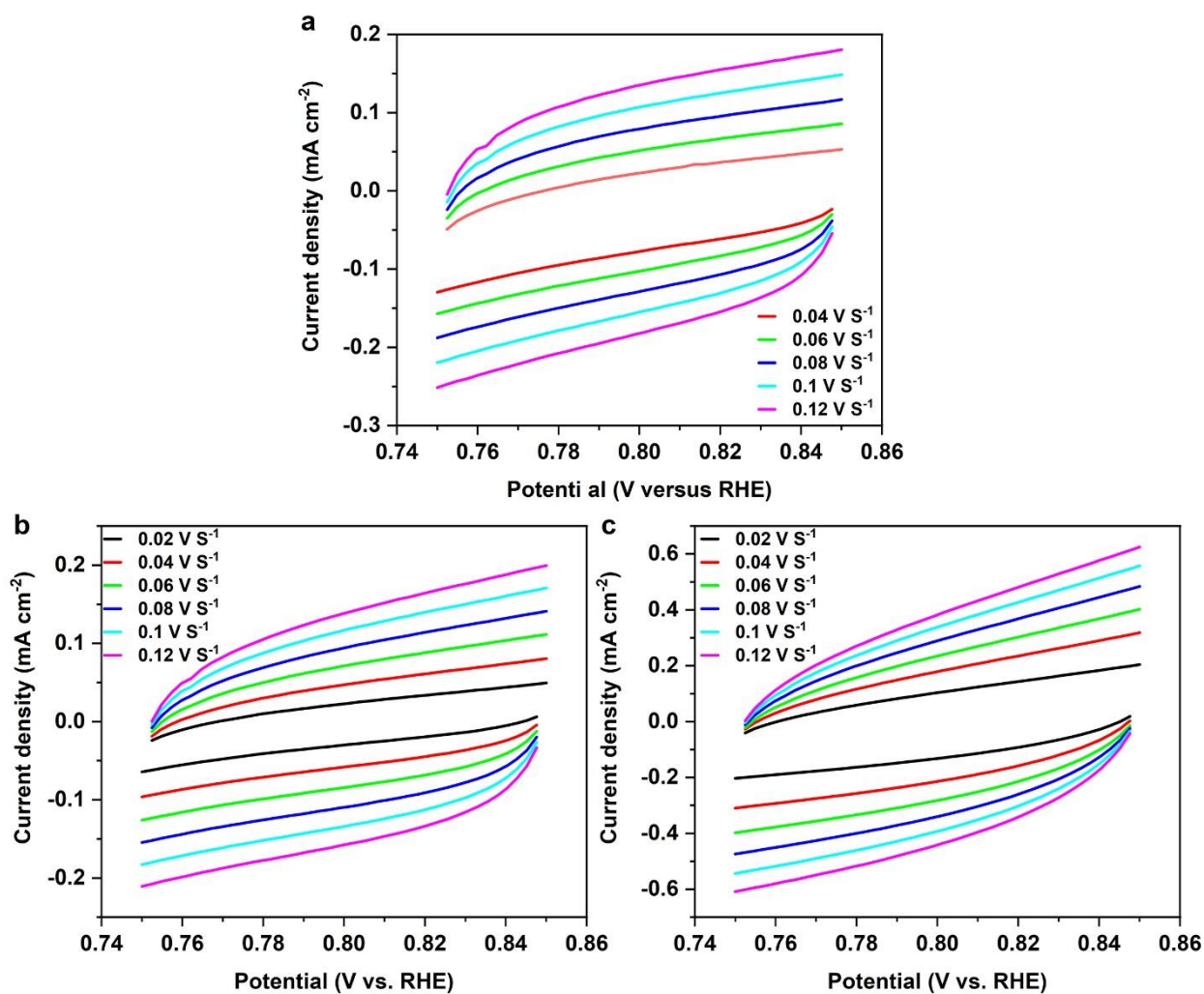


Figure D8. Typical cyclic voltammetry (CV) curves obtained at different scan rates ($0.02\text{--}0.12\text{ V s}^{-1}$) within the potential window $0.75\text{--}0.85\text{ V}$ vs RHE for a) NiMo, b) CoMoO₄, and c) NiMo/CoMoO₄.

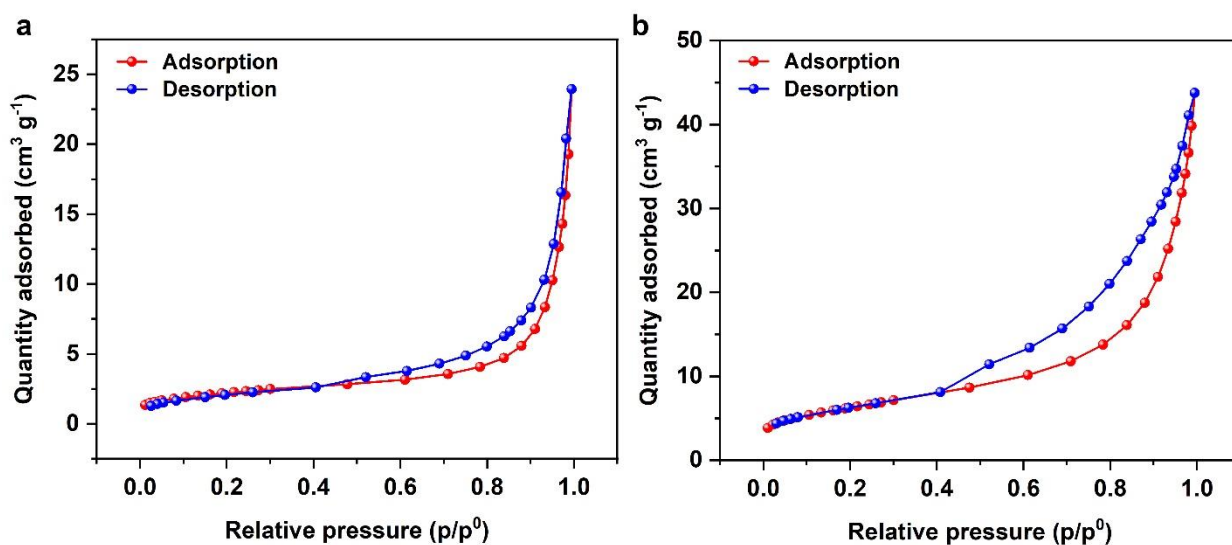


Figure D9. N₂ adsorption-desorption isotherms of a) CoMoO₄ and b) NiMo/CoMoO₄.

Table D 1. The HER performances of recent reports on NiMo-derivative catalysts in terms of overpotential at 10 mA cm⁻² (η^{10}) current density.

Sample	Electrolyte	η_{HER} (mV)	Ref.
Ni _{0.99} Mo _{0.01}	KOH	$\eta^{10} = 242$	[314]
Ni ₉ Mo ₁	KOH	$\eta^{10} = 159$	[54]
Ni ₃ Mo ₇		$\eta^{10} = 86$	
NiMo@MoS ₂	KOH	$\eta^{10} = 89$	[315]
NiMo/Ti mesh	KOH	$\eta^{10} = 92$	[59]
NiMo	KOH	$\eta^{10} = 157$	[316]
NiMo	KOH	$\eta^{10} = 220$	[317]
NiMo@C ₃ N ₅		$\eta^{10} = 82$	
NiMo–NiCu	KOH	$\eta^{10} = 86$	[318]
NiMo/Ni(OH) ₂ /CC	KOH	$\eta^{10} = 132$	[319]
NiMo-porous	KOH	$\eta^{10} = 117$	[320]
MoNi ₄ -MX10	KOH	$\eta^{10} = 122.2$	[321]
Ni-Mo-Fe	KOH	$\eta^{10} = 65$	[322]
NiFeMo/SSM	KOH	$\eta^{10} = 86$	[323]
Ni-Mo-Cu	KOH	$\eta^{10} = 49$	[324]
Ni-Mo-Co	KOH	$\eta^{10} = 108$	[325]
NiMo/CoMoO ₄ on NF	KOH	$\eta^{10} = 102$	This work

Table D 2. Fit parameters from the equivalent circuit for NiMo.

Overpotential (mV)	R_s (Ω)	R_p (Ω)	CPE-T (F⁻¹ s¹⁻ⁿ)	R_{ct} (Ω)	C_{dl}-T (F⁻¹ s¹⁻ⁿ)
0	2.173	97.32	0.00036722	244.8	0.0025991
100	2.176	21.89	0.00058292	60.49	0.00091167
110	2.226	17.2	0.0011342	74.13	0.00062283
120	2.211	14.51	0.0016228	75.41	0.00058142
130	2.208	11.25	0.0025679	70.64	0.00050919
140	2.2	9.612	0.0027226	59.63	0.00051521
150	2.179	4.551	0.0038622	53.2	0.0005098
160	2.158	6.81	0.0023461	42.82	0.00048663
170	2.158	4.915	0.001666	34.72	0.00049196
180	2.154	3.203	0.0019365	29.6	0.00053691
190	2.143	7.76	0.0010404	19.37	0.00047623
200	2.134	5.302	0.0015859	17.14	0.00061359

Table D 3. . Fit parameters from the equivalent circuit for CoMoO₄.

Overpotential (mV)	R_s (Ω)	R_p (Ω)	CPE-T (F⁻¹ s¹⁻ⁿ)	R_{ct} (Ω)	C_{dl}-T (F⁻¹ s¹⁻ⁿ)
0	2.56	41.47	0.0028626	463	0.0022426
100	2.517	48.69	0.002588	198.9	0.0032955
110	2.474	46.54	0.0025965	160.7	0.0035705
120	2.458	39.19	0.0027978	143.9	0.0037863
130	2.448	26.81	0.0035169	133.3	0.003827
140	2.442	19.83	0.0040219	104.5	0.0036551
150	2.439	18.96	0.0043158	76.41	0.0037322
160	2.44	5.128	0.0079495	66.97	0.00272
170	2.458	0.37252	0.0034486	55.18	0.0024631
180	2.462	0.36819	0.003346	44.33	0.002455
190	2.481	1.278	0.005298	33.15	0.0022328
200	2.478	1.768	0.0078852	24.69	0.0023678

Table D 4. Fit parameters from the equivalent circuit for NiMo/CoMoO₄.

Overpotential (mV)	R_s (Ω)	R_p (Ω)	CPE-T (F⁻¹ s¹⁻ⁿ)	R_{ct} (Ω)	C_{dl}-T (F⁻¹ s¹⁻ⁿ)
0	2.365	0.74985	0.037549	301.5	0.034138
100	2.4	0.641	0.018319	336.5	0.042951
110	2.374	0.63787	0.018345	277.9	0.042917
120	2.38	0.5691	0.013569	247.2	0.043461
130	2.393	0.52911	0.0096549	215.5	0.043401
140	2.396	0.50808	0.0083058	167.1	0.043154
150	2.395	0.4853	0.0075476	129.9	0.043588
160	2.39	0.4923	0.0085399	97.96	0.043811
170	2.374	0.52497	0.012046	77.24	0.044553
180	2.37	0.56593	0.015104	59.73	0.045069
190	2.366	0.5926	0.017162	48.3	0.045239
200	2.354	0.6747	0.023006	37.78	0.044946

Table D 5. Further details derived from BET analysis of the samples.

Sample	BET Surface Area (m²/g)	Micropore Area (m²/g)	External Surface Area (m²/g)	Micropore Volume (cm³/g)
CoMoO₄	7.7504	0.7526	6.9978	0.000360
NiMo/CoMoO₄	22.223	1.5308	20.6930	0.000659

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Appendix E

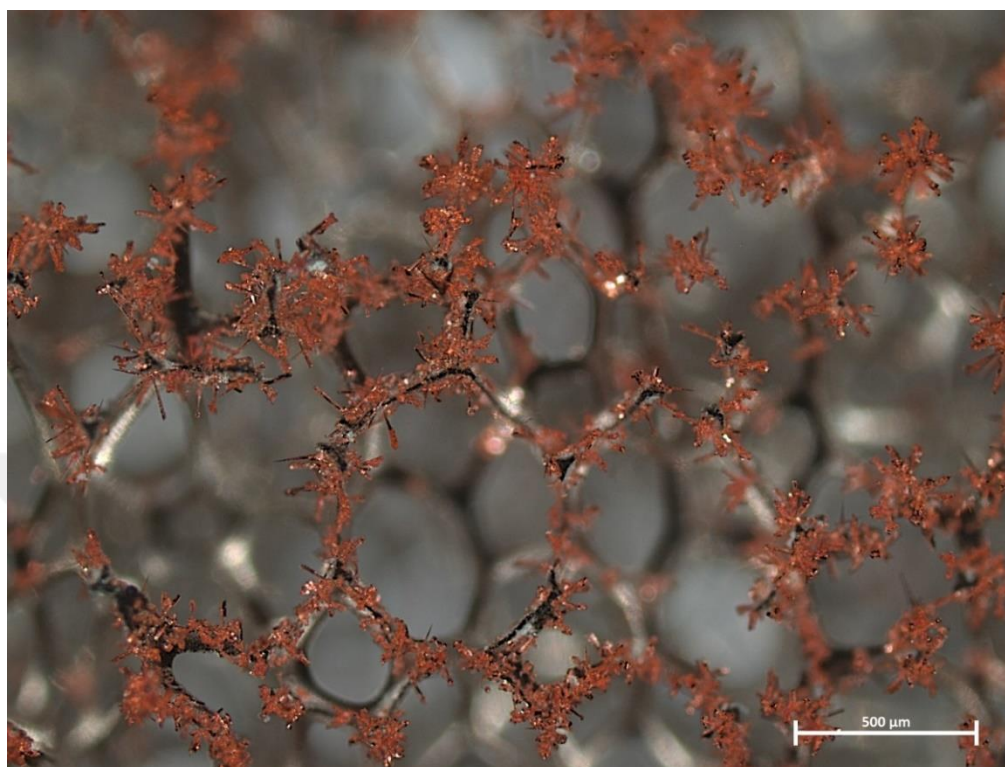


Figure E1. Polarized optical microscope image of Cu-coated NF using electrodeposition method.

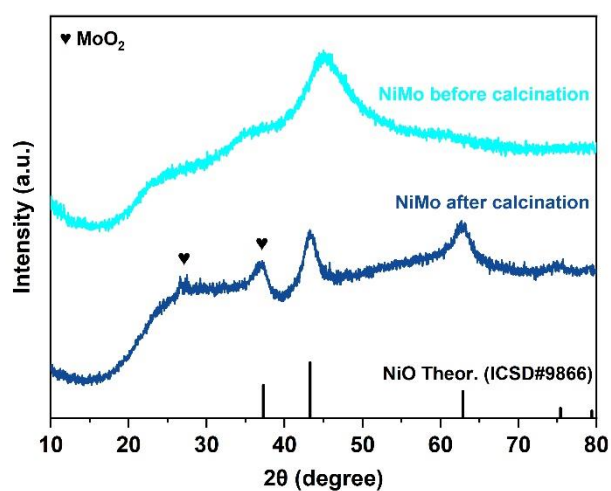


Figure E2. XRD patterns of NiMo nanoparticles before and after calcination process at 500 °C under air.

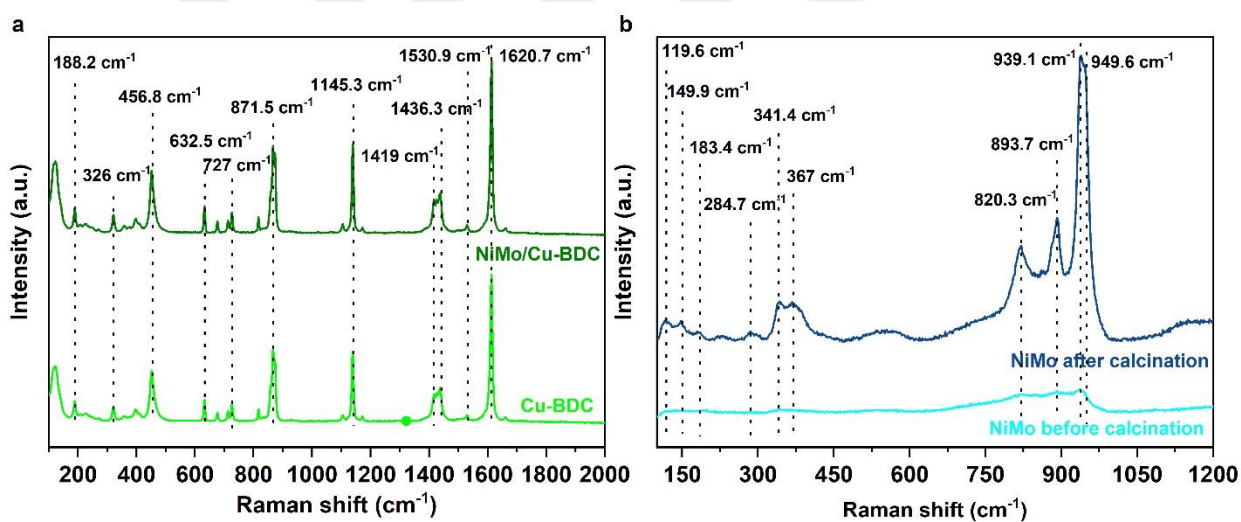


Figure E3. Raman spectra for a) Cu-BDC and NiMo/Cu-BDC and b) NiMo nanoparticles before and after calcination process at 500 °C under air.

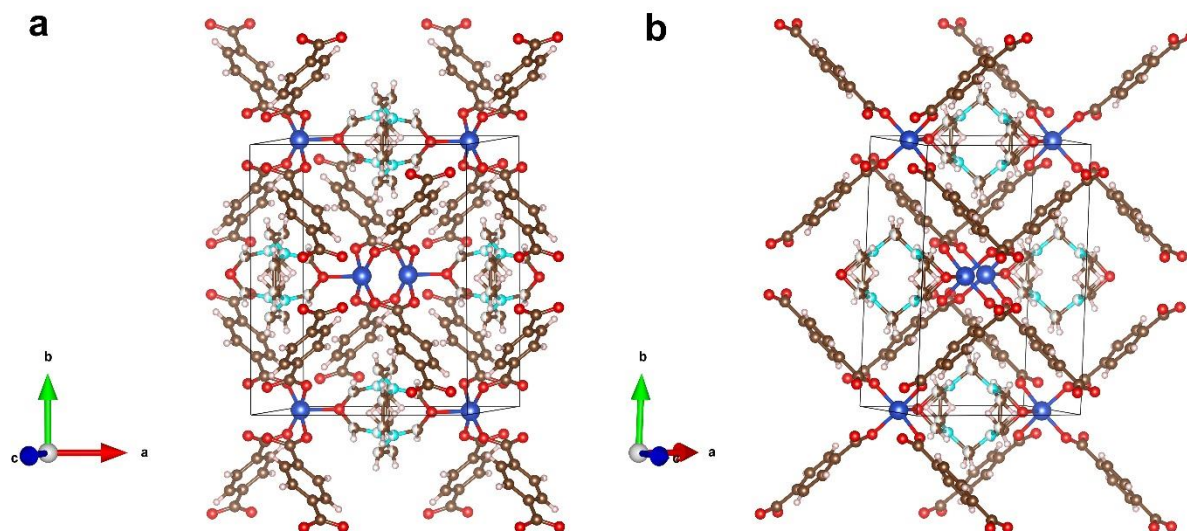


Figure E4. a and b) Crystal structures of Cu-BDC MOF from two perspectives, Cu (dark blue), C (dark brown), H (pink), O (red), and N (light blue).

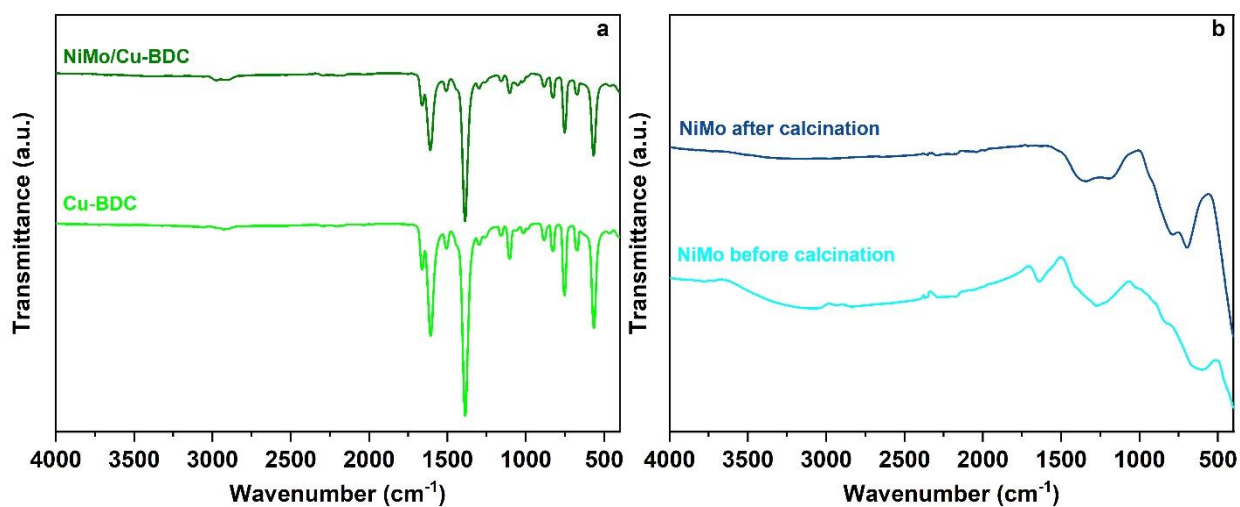


Figure E5. Ft-IR spectra for a) Cu-BDC and NiMo/Cu-BDC and b) NiMo nanoparticles before and after calcination process at 500 °C under air.

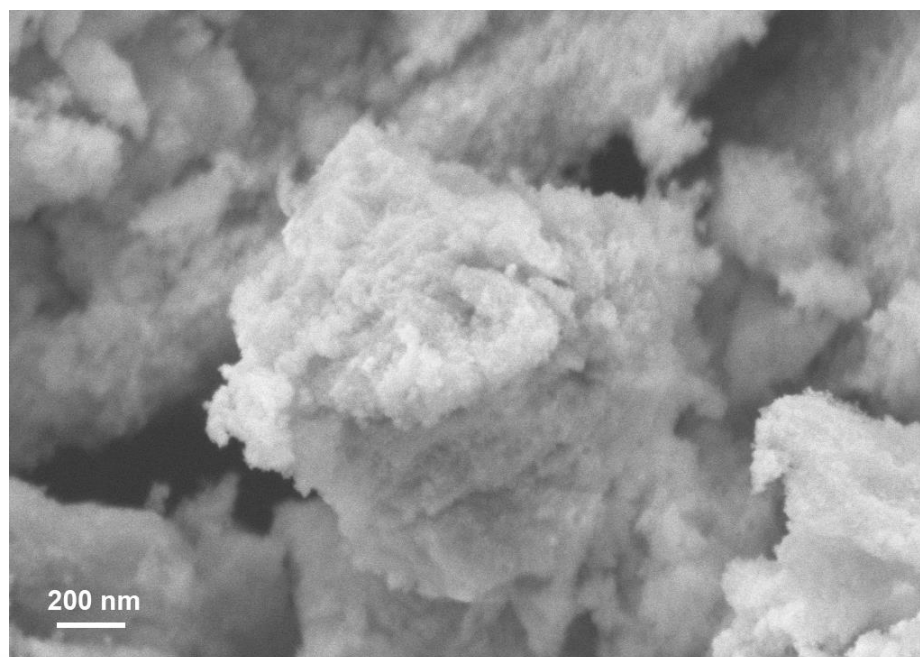


Figure E6. SEM image of NiMo nanoparticles before calcination process.

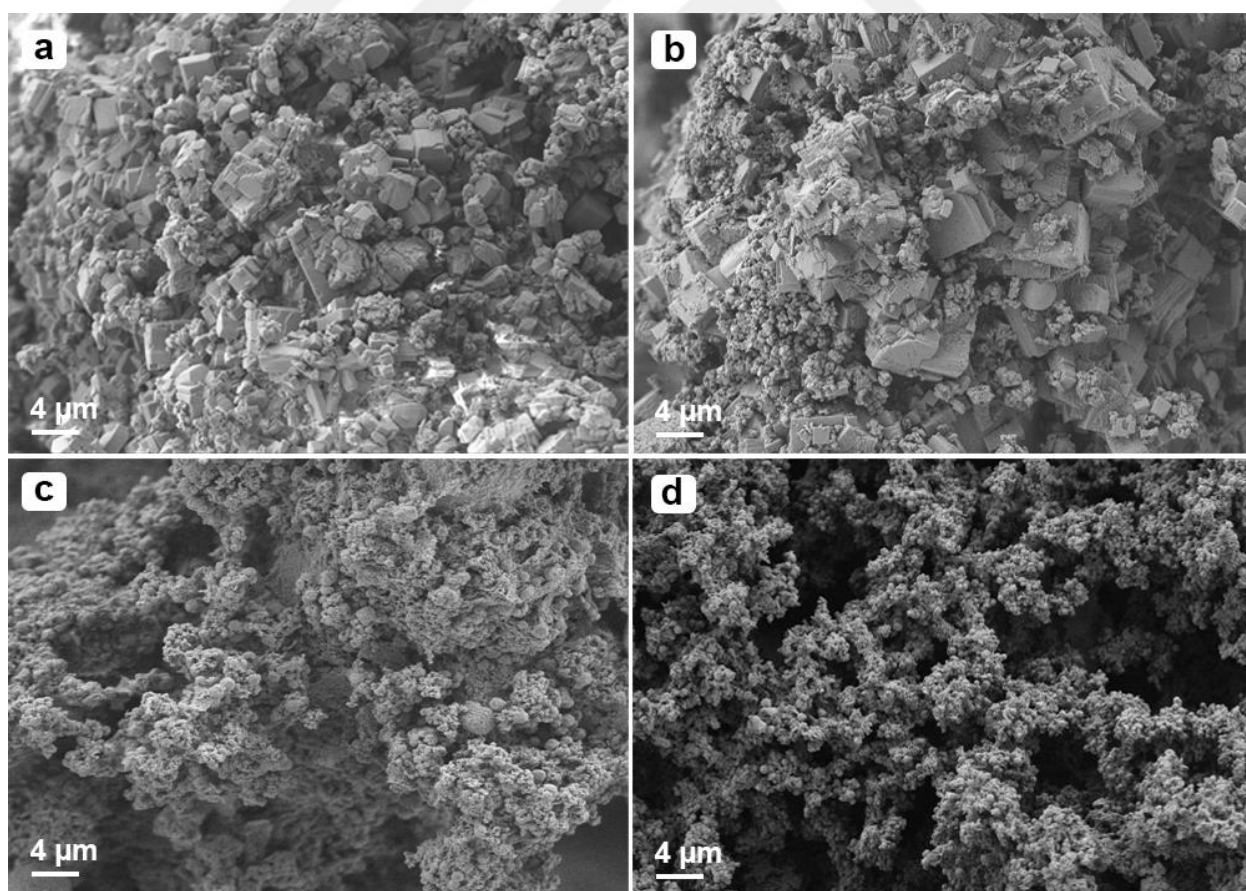


Figure E7. Illustration of uniform growth of catalysts on the backbone of NF substrate.
a) Cu-BDC, b) Cu-BDC_{Cal.}, c) NiMo/Cu-BDC, and d) NiMo/Cu-BDC_{Cal.}

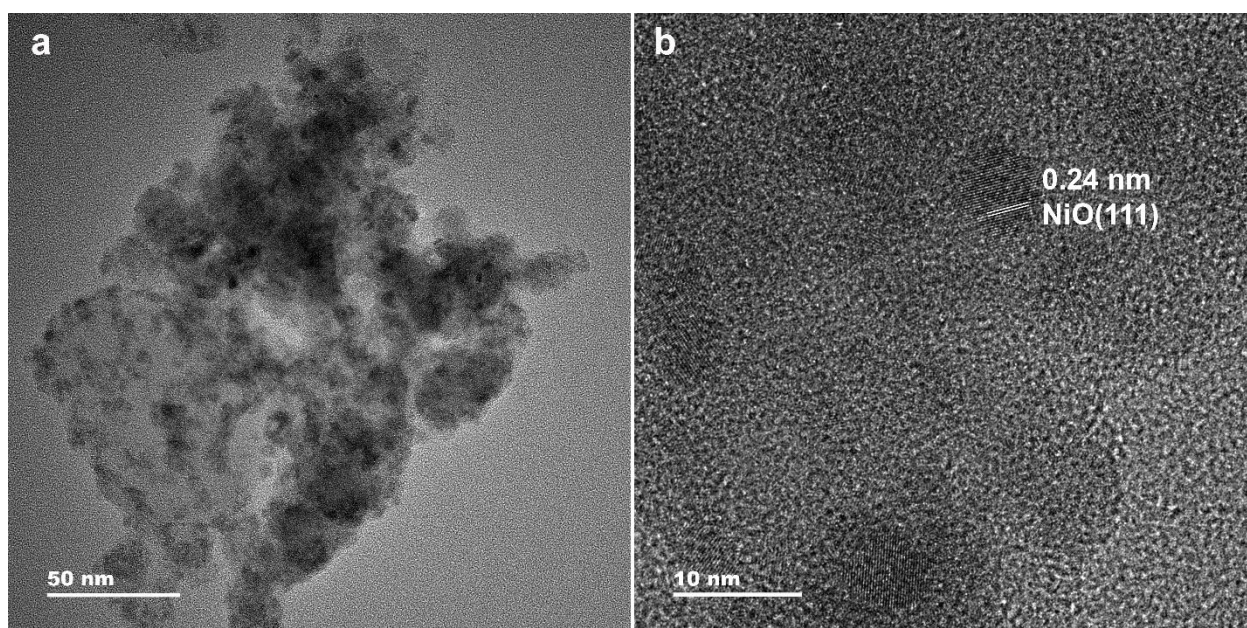


Figure E8. a) TEM and b) HR-TEM images of NiMo after calcination process at 500 °C under air.

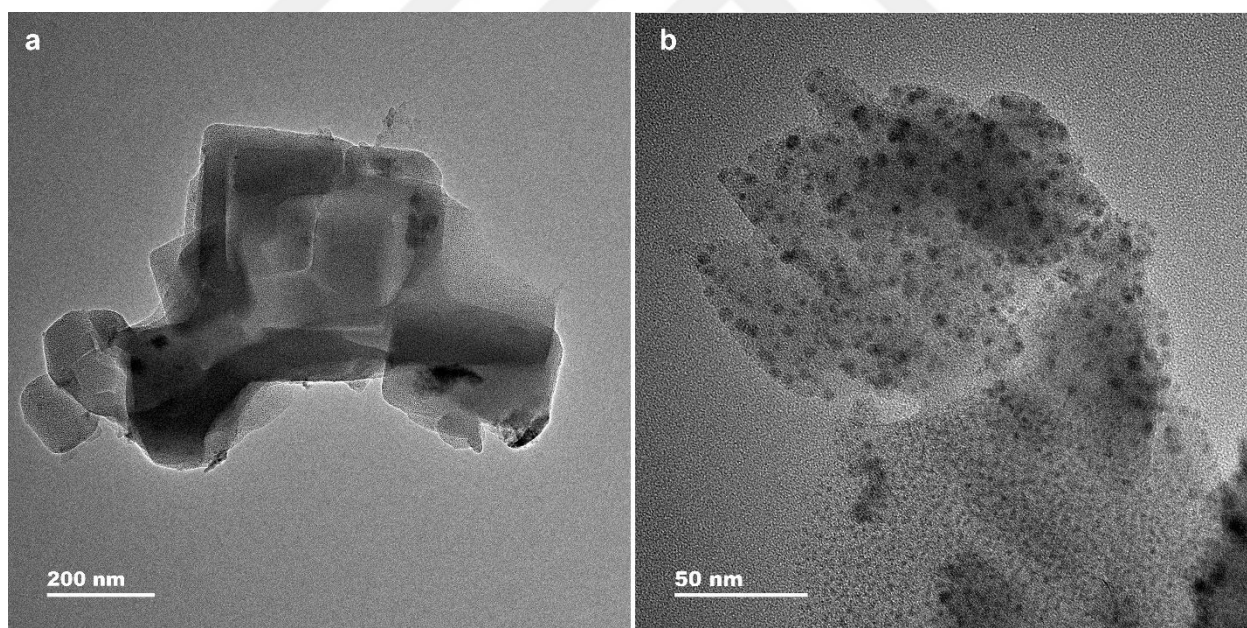


Figure E9. a) TEM and b) HR-TEM images of NiMo/Cu-BDC.

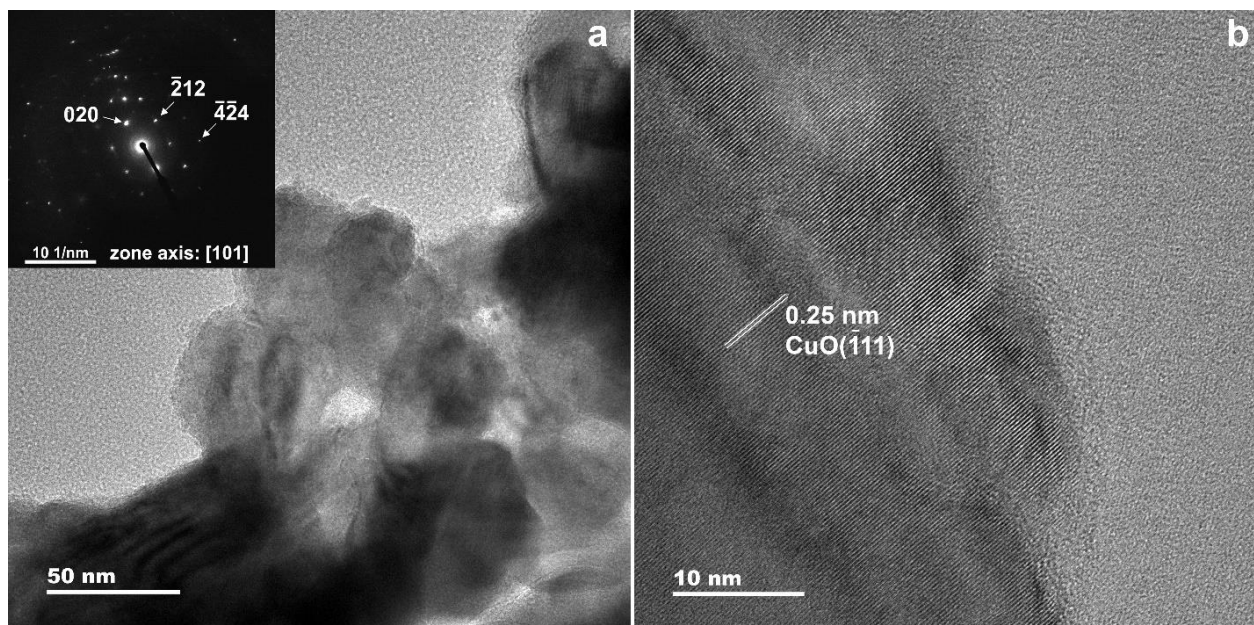


Figure E10. a) TEM and b) HR-TEM images of Cu-BDC_{Cal}. (inset: SAED image).

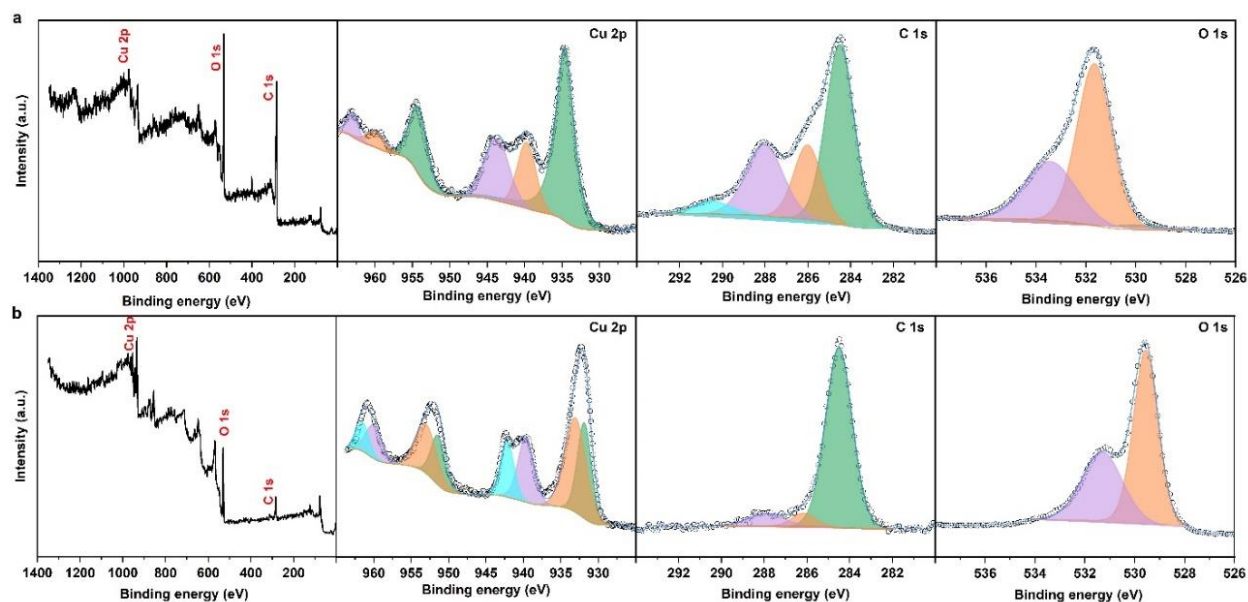


Figure E11. XPS spectra including survey, Cu 2p, C 1s, and O 1s for a) Cu-BDC and b) Cu-BDC_{Cal}.

Table E 1. Fit parameters from the equivalent circuit for as-fabricated electrodes.

Sample	R_s (Ω)	R_p (Ω)	CPE-T ($F^{-1} s^{1-n}$)	R_{ct} (Ω)	C_{dl-T} ($F^{-1} s^{1-n}$)
Cu-BDC	3.508	12.69	0.21038	7.242	0.068377
Cu-BDC_{Cal.}	2.767	6.653	0.030981	4.146	0.48013
NiMo/Cu-BDC	2.6	7.19	0.030728	6.211	0.54241
NiMo/Cu-BDC_{Cal.}	2.524	6.282	0.032484	2.608	0.21292

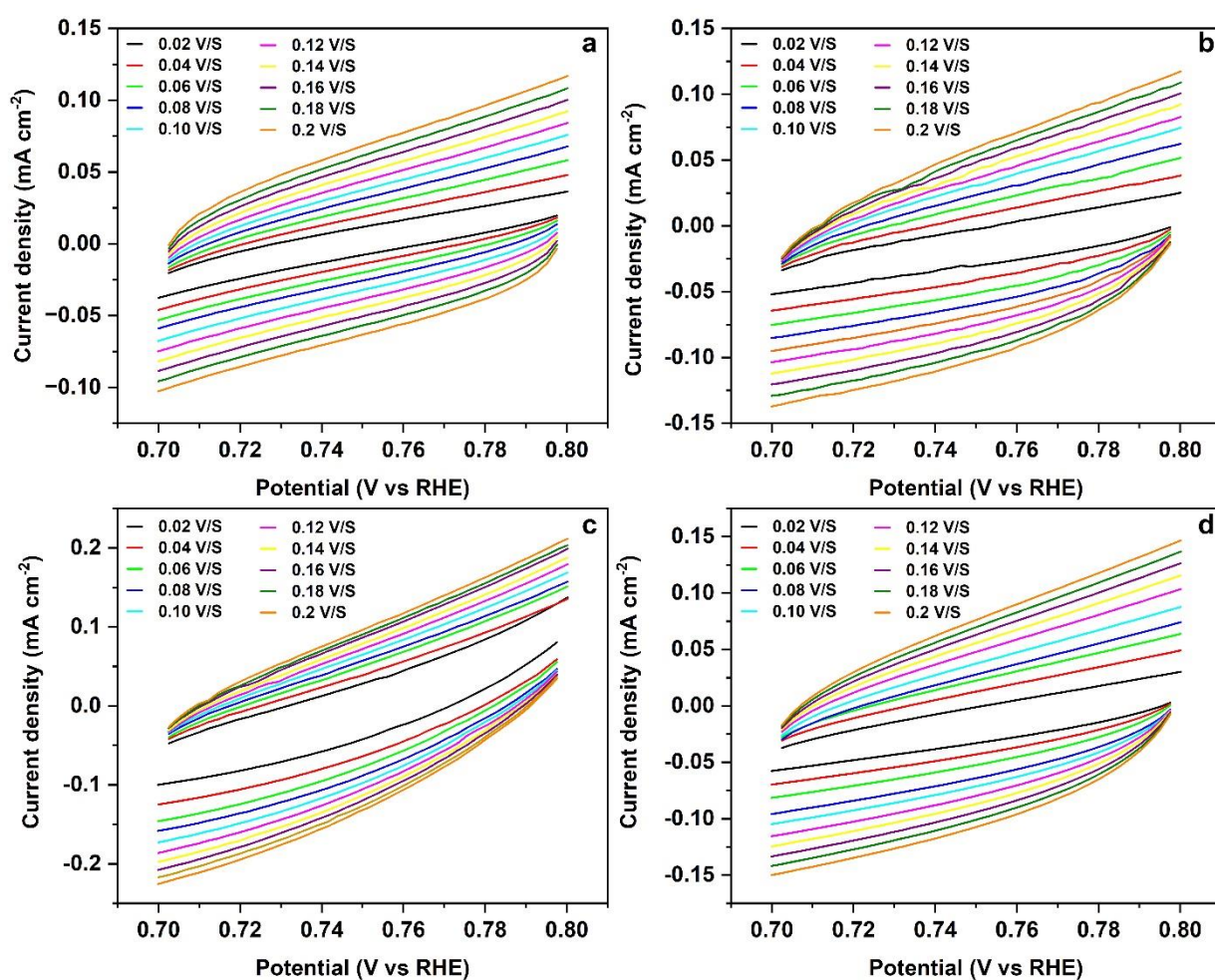


Figure E12. Typical cyclic voltammetry (CV) curves obtained at different scan rates (0.02–0.2 V s⁻¹) within the potential window 0.7–0.8 V vs RHE for a) Cu-BDC, b) Cu-BDC_{Cal.}, c) NiMo/Cu-BDC, and d) NiMo/Cu-BDC_{Cal.}.

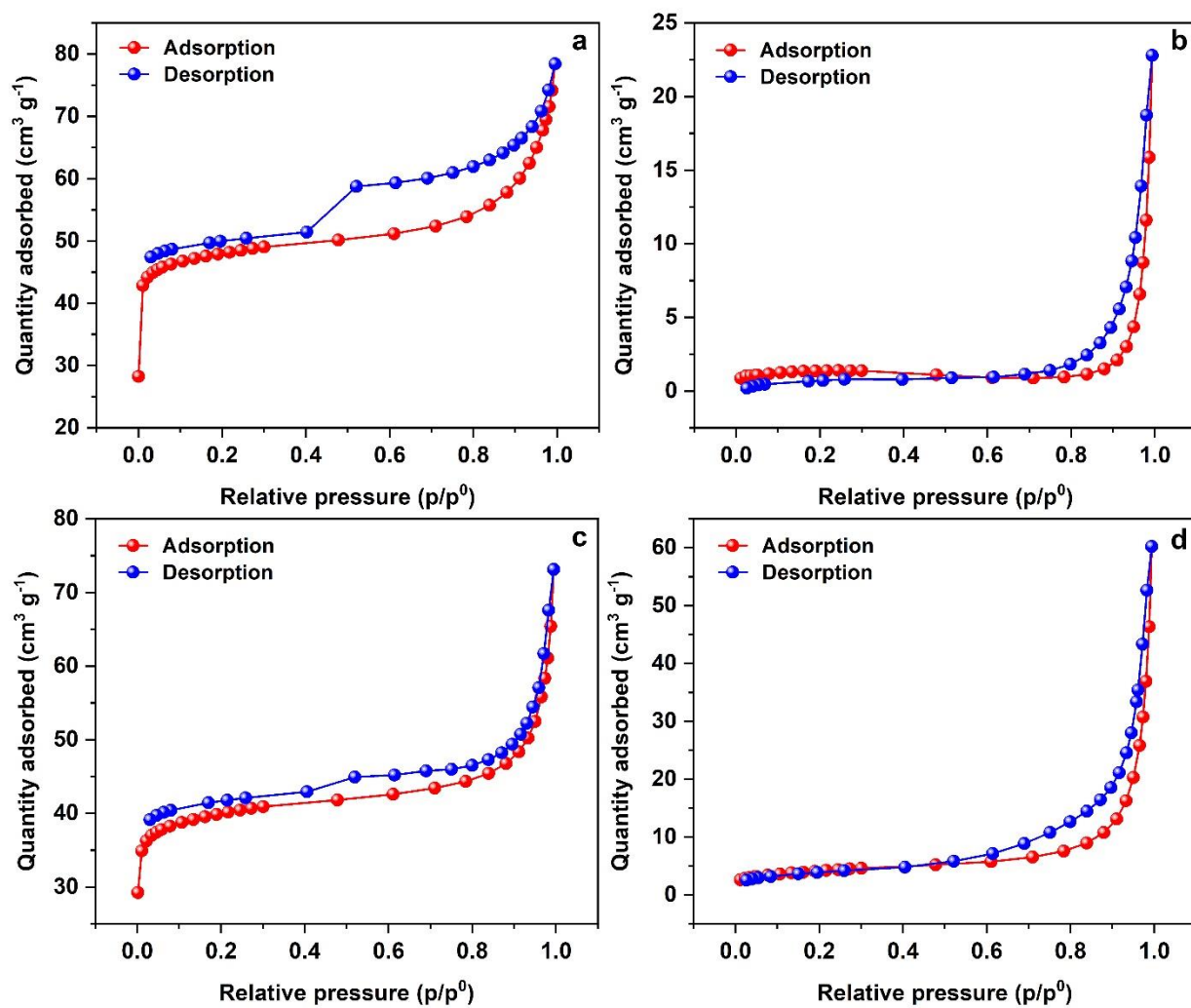


Figure E13. N_2 adsorption-desorption isotherms of a) Cu-BDC, b) Cu-BDC_{Cal.}, c) NiMo/Cu-BDC, and d) NiMo/Cu-BDC_{Cal.}.

Table E 2. Further details derived from BET analysis of the samples.

Sample	BET Surface Area (m ² /g)	Micropore Area (m ² /g)	External Surface Area (m ² /g)	Micropore Volume (cm ³ /g)
Cu-BDC	146.88	117.99	28.88	0.061
Cu-BDC_{Cal.}	4.26	2.49	1.77	0.001
NiMo/Cu-BDC	122.74	94.59	28.15	0.049
NiMo/Cu-BDC_{Cal.}	14.37	1.99	12.37	0.0009



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