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Cobalt-based Nanocatalysts for Electrochemical Energy Conversion

Xiang Wang



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Tesi doctoral

Cobalt-based Nanocatalysts for Electrochemical Energy Conversion

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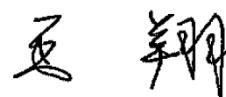
Cobalt-based Nanocatalysts for Electrochemical Energy Conversion

Memòria presentada per optar al grau de doctor per la
Universitat de Barcelona

Programa de doctorat en Nanociències

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Barcelona, Spain

March, 2022

List of Publications

The research work during my PhD period can be included in three peer-reviewed publications. The full copy of each of the publications can be found in the Annex part at the end of the thesis. The list of the publication is shown as follows:

1. **Wang, X.**; Xing, C.; Liang, Z.; Guardia, P.; Han, X.; Zuo, Y.; Llorca, J.; Arbiol, J.; Li, J.; Cabot, A., Activating the lattice oxygen oxidation mechanism in amorphous molybdenum cobalt oxide nanosheets for water oxidation. *Journal of Materials Chemistry A* **2022**, 10(7), 3659-3666.
2. **Wang, X.**; Yang, L.; Xing, C.; Han, X.; Du, R.; He, R.; Guardia, P.; Arbiol, J.; Cabot, A., MOF-derived ultrathin cobalt molybdenum phosphide nanosheets for efficient electrochemical overall water splitting. *Nanomaterials* **2022**, 12(7), 1098.
3. Li, J.; **Wang, X.**; Xing, C.; Li, L.; Mu, S.; Han, X.; He, R.; Liang, Z.; Martinez, P.; Yi, Y., Electrochemical Reforming of Ethanol with Acetate Co-Production on Nickel Cobalt Selenide Nanoparticles. *Chemical Engineering Journal* **2022**, 135817.

Apart from the publication listed above, I also contributed to some other projects during my PhD period, which are not shown in this thesis. Some of these publications are listed below:

4. Liang, Z.; Jiang, D.; **Wang, X.**; Shakouri, M.; Zhang, T.; Li, Z.; Tang, P.; Llorca, J.; Liu, L.; Yuan, Y., Molecular Engineering to Tune the Ligand Environment of Atomically Dispersed Nickel for Efficient Alcohol Electrochemical Oxidation. *Advanced Functional Materials* **2021**, 31 (51), 2106349.
5. Zhang, Y.; Xing, C.; Liu, Y.; Spadaro, M. C.; **Wang, X.**; Li, M.; Xiao, K.; Zhang, T.; Guardia, P.; Lim, K. H., Doping-mediated stabilization of copper vacancies to promote thermoelectric properties of Cu_{2-x}S . *Nano Energy* **2021**, 85, 105991.
6. Xing, C.; Zhang, Y.; Liu, Y.; **Wang, X.**; Li, J.; Martínez-Alanis, P. R.; Spadaro, M. C.; Guardia, P.; Arbiol, J.; Llorca, J., Photodehydrogenation of ethanol over $\text{Cu}_2\text{O}/\text{TiO}_2$ heterostructures. *Nanomaterials* **2021**, 11 (6), 1399.
7. Zhang, C.; Du, R.; Biendicho, J. J.; Yi, M.; Xiao, K.; Yang, D.; Zhang, T.; **Wang, X.**; Arbiol, J.; Llorca, J., Tubular CoFeP@CN as a Mott-Schottky Catalyst with

- Multiple Adsorption Sites for Robust Lithium– Sulfur Batteries. *Advanced Energy Materials* **2021**, *11* (24), 2100432.
8. Liang, Z.; Yang, D.; Tang, P.; Zhang, C.; Jacas Biendicho, J.; Zhang, Y.; Llorca, J.; **Wang, X.**; Li, J.; Heggen, M., Atomically dispersed Fe in a C₂N based catalyst as a sulfur host for efficient lithium–sulfur batteries. *Advanced energy materials* **2021**, *11* (5), 2003507.
 9. Xing, C.; Liu, Y.; Zhang, Y.; **Wang, X.**; Guardia, P.; Yao, L.; Han, X.; Zhang, T.; Arbiol, J.; Soler, L., A direct Z-scheme for the photocatalytic hydrogen production from a water ethanol mixture on CoTiO₃/TiO₂ heterostructures. *ACS Applied Materials & Interfaces* **2021**, *13* (1), 449-457.
 10. Li, J.; Wei, R.; **Wang, X.**; Zuo, Y.; Han, X.; Arbiol, J.; Llorca, J.; Yang, Y.; Cabot, A.; Cui, C., Selective Methanol-to-Formate Electrocatalytic Conversion on Branched Nickel Carbide. *Angewandte Chemie* **2020**, *132* (47), 21012-21016.
 11. Zuo, Y.; Xu, X.; Zhang, C.; Li, J.; Du, R.; **Wang, X.**; Han, X.; Arbiol, J.; Llorca, J.; Liu, J., SnS₂/g-C₃N₄/graphite nanocomposites as durable lithium-ion battery anode with high pseudocapacitance contribution. *Electrochimica Acta* **2020**, *349*, 136369.
 12. Zuo, Y.; Li, J.; Yu, X.; Du, R.; Zhang, T.; **Wang, X.**; Arbiol, J.; Llorca, J.; Cabot, A., A SnS₂ molecular precursor for conformal nanostructured coatings. *Chemistry of materials* **2020**, *32* (5), 2097-2106.
 13. Yu, X.; Luo, Z.; Zhang, T.; Tang, P.; Li, J.; **Wang, X.**; Llorca, J.; Arbiol, J.; Liu, J.; Cabot, A., Stability of Pd₃Pb nanocubes during electrocatalytic ethanol oxidation. *Chemistry of Materials* **2020**, *32* (5), 2044-2052.
 14. Li, J.; Xu, X.; Yu, X.; Han, X.; Zhang, T.; Zuo, Y.; Zhang, C.; Yang, D.; **Wang, X.**; Luo, Z., Monodisperse CoSn and NiSn nanoparticles supported on commercial carbon as anode for lithium-and potassium-ion batteries. *ACS applied materials & interfaces* **2020**, *12* (4), 4414-4422.
 15. Li, J.; Zuo, Y.; Liu, J.; **Wang, X.**; Yu, X.; Du, R.; Zhang, T.; Infante-Carrió, M. F.; Tang, P.; Arbiol, J., Superior methanol electrooxidation performance of (110)-faceted nickel polyhedral nanocrystals. *Journal of Materials Chemistry A* **2019**, *7* (38), 22036-22043.
 16. Li, J.; **Wang, X.**; Xing, C.; Li, L.; Mu, S.; Han, X.; He, R.; Liang, Z.; Martinez, P.; Yi, Y., Electrochemical Reforming of Ethanol with Acetate Co-Production on Nickel Cobalt Selenide Nanoparticles. *Chemical Engineering Journal* **2022**, 135817.

Authors' Contributions

All work and results presented in this thesis were carried out in the Functional Nanomaterials group of Catalonia Institute for Energy Research (IREC) under the supervision of prof. Andreu Cabot. None of the publications in this thesis have been previously presented in any other PhD thesis. The thesis author, Xiang Wang, contributed to the main part of the work, including experiment design, material synthesis, electrochemical measurements, data analysis and original paper writing in this thesis. Prof. Andreu Cabot conceived and guided the project, significantly participated in the results discussion and manuscript corrections. The contribution of co-author for each publication are shown below, as well as the impact factor in 2020/201 of each journal where the manuscript was published.

Chapter 2:

Wang, X.; Xing, C.; Liang, Z.; Guardia, P.; Han, X.; Zuo, Y.; Llorca, J.; Arbiol, J.; Li, J.; Cabot, A., Activating the lattice oxygen oxidation mechanism in amorphous molybdenum cobalt oxide nanosheets for water oxidation. *Journal of Materials Chemistry A* 2022, 10, 3659-3666.

Impact Factor 2020/21: 12.74

In this work, X. Wang designed the experiments, produced the nanoparticles, conducted XRD, BET, SEM-EDX characterization, oxygen evolution reaction measurements, and wrote the first draft of the manuscript. C. Xing, Z. Liang, P. Guardia and Y. Zuo significantly contributed to the results discussion. P. Guardia carried out the TEM measurements. X. Han, and J. Arbiol performed structural and compositional characterization by means of HRTEM and EELS, and discussed the results. C. Xing and J. Llorca measured and discussed XPS, Raman data. J. Li carried out the *in-situ* Raman measurements and discussed the results. A. Cabot conceived and guided the project, and supervised the work. The manuscript was corrected and improved by all authors.

Chapter 3:

Wang, X., Li, J., Han, X., Xing, C., Liang, Z., Guardia, P., Zuo, Y., Du, R., Balcells, L., J. Arbiol, J. Llorca, A. Cabot. Sulfate-decprated amorphous-crystalline cobalt-iron oxide nanosheets to enhance O-O coupling in the oxygen evolution reaction. Submitted

In this work, X. Wang designed the experiments, produced the nanocatalysts, conducted XRD, BET, SEM-EDX and FT-IR characterization, electrochemical measurements, and wrote the first draft of the manuscript. C. Xing and Z. Liang significantly contributed to the results discussion. P. Guardia carried out the TEM measurements. X. Han and J. Arbiol performed structural and compositional characterization by means of HRTEM and EELS, and discussed the results. C. Xing and J. Llorca measured and discussed Raman and XPS data. J. Li carried out the in-situ Raman measurements and discussed the results. A. Cabot conceived and guided the project, and supervised the work. The manuscript was corrected and improved by all authors.

Chapter 4:

Wang, X.; Yang, L.; Xing, C.; Han, X.; Du, R.; He, R.; Guardia, P.; Arbiol, J.; Cabot, A., MOF-derived ultrathin cobalt molybdenum phosphide nanosheets for efficient electrochemical overall water splitting. *Nanomaterials* 2022.

Impact Factor 2020/21: 5.07

In this work, X. Wang designed the experiments, produced the nanocatalysts, conducted XRD, XPS, SEM-EDX characterization, electrochemical measurements, and wrote the first draft of the manuscript. L. Yang, R. Du, C. Xing and R. He contributed to the results discussion and improvement. P. Guardia carried out the TEM measurements. X. Han and J. Arbiol performed structural and compositional characterization by means of HRTEM and EELS, and discussed the results. A. Cabot conceived and guided the project, and supervised the work. The manuscript was corrected and improved by all authors.

Chapter 5:

Li, J.; **Wang, X.**; Xing, C.; Li, L.; Mu, S.; Han, X.; He, R.; Liang, Z.; Martinez, P.; Yi, Y., Electrochemical Reforming of Ethanol with Acetate Co-Production on Nickel Cobalt Selenide Nanoparticles. *Chemical Engineering Journal* 2022, 135817.

In this work, J. Li designed the experiments, produced the catalysts, conducted XRD, SEM-EDX, XPS characterizations and wrote the first draft of the manuscript. X. Wang conducted the electrochemical measurements. C. Xing, L. Li, S. Mu, R. He, Z. Liang, P. Martinez, Y. Li, Q. Wu significantly contributed to the results discussion. X. Han and J. Arbiol performed structural and compositional characterization by means of HRTEM and EELS, and discussed the results. A. Cabot, C. Cui, Y. Zhang conceived and guided the project, and supervised the work. The manuscript was corrected and improved by all authors.

Prof. Andreu Cabot



had certified the information provided above was true.

Barcelona, March, 2022

Preface

The research work in this thesis was carried out by the PhD candidate of Xiang Wang in the Functional Nanomaterials at Catalonia Institute for Energy Research (IREC) in the period 2018-2022 under the supervision of Prof. Andreu Cabot. This thesis is focused on the synthesis of cobalt-based nanocatalysts and their application in three key electrochemical energy conversion reactions/technologies: oxygen evolution, overall water splitting, and hydrogen evolution from alcohol oxidation.

This thesis consists of 5 chapters. In the first chapter, a general introduction of the background, motivations and objectives of this thesis is presented. The experimental work performed to achieve these objectives is shown in Chapters 2 to 5. In these four chapters, four kinds of cobalt-based nanocatalysts, namely MoCo_xO_y (chapter 2), $\text{CoFe}_x\text{O}_y\text{-SO}_4$ (chapter 3) and CoMoP (chapter 4) and NiCoSe (chapter 5), have been produced through an ion etching and pyrolysis assisted strategy and applications in electrochemical oxygen evolution (first block: chapter 2 and 3), electrochemical water splitting (second block: chapter 4), and electrochemical ethanol oxidation (third block: chapter 5) have been investigated.

The first block includes chapters 2 and 3 and it is dedicated to the oxygen reactions. In this block, an ion etching and pyrolysis assisted strategy using cobalt-based ZIF-67 as self-sacrificial template and a metal ammonium salt as metal precursor and etching agent is detailed to produce MoCo_xO_y and $\text{CoFe}_x\text{O}_y\text{-SO}_4$. Meanwhile In this block, in situ Raman technology was applied to explore the catalytic reaction process during the oxygen evolution reaction (OER).

The second block, chapter 4, is devoted to the overall water splitting reaction. For these electrochemical applications, bifunctional CoMoP nanosheets are produced using the Co-MOF ZIF-67 as a self-sacrificial template and ammonium molybdate as a shape-defining agent and Mo source.

The third block, chapter 5, is focused on the hydrogen evolution through the ethanol oxidation reaction (EOR). For this electrochemical application, and particularly the EOR side, I detail here a solution-based method to produce $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$ NPs with tuned metal ratios, where CoSe_2 showed enhanced OER activity and NiSe_2 demonstrated a more

efficient EOR. The incorporation of small amounts of Co to the NiSe₂ structure resulted in the highest EOR activities.

After the experimental chapters, four chapters of results, discussion of results, conclusions and outlook are included, and the CV of the author is also attached at the end of the thesis.

Summary of Results

Cobalt-based nanomaterials are an important class of electrocatalysts that own abundant and diverse d-orbital electronic structures, and can exhibit excellent HER, OER, EOR catalytic activity and stability in energy conversion. Despite some elemental cobalt catalysts having been recognized as potential candidate catalysts in some reactions, the performance of elemental cobalt is far from ideal, especially in the field of electrocatalysis. Thus, composite cobalt-based nanocatalysts have been developed by introducing other materials such as carbon to increase surface area and electrical conductivity, and transition metal elements that allow a fine-tuning of the Co electronic energy levels. In my thesis, I detail the synthesis and performance of four cobalt-based nanocatalysts, namely MoCo_xO_y , $\text{CoFe}_x\text{O}_y\text{-SO}_4$, CoMoP and $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$, towards three key electrochemical energy conversion processes, namely electrochemical oxygen evolution, overall water splitting and hydrogen evolution from ethanol oxidation.

In the first chapter, a general introduction to the relevant electrochemical energy conversion technologies and cobalt-based nanocatalysts is presented to explain the motivation of this thesis.

In Chapter 2, I detail the case of amorphous ultrathin MoCo_xO_y nanosheets with excellent OER catalytic performance and prepared through an ion etching and pyrolysis assisted strategy. The incorporation of molybdate ions not only modifies the material architecture to generate two-dimensional layered nanosheet structures, but also regulates the local coordination environment and electronic structure of the cobalt oxide. The incorporation of molybdenum introduces abundant vacancies and oxygen adsorbed species. Besides, the amorphous nanosheet architecture of the material favors the presence of surface defects and coordinatively unsaturated sites, boosting the exposure of active sites and further improving catalytic activity. Finally, using several pieces of evidence revealed the incorporation of molybdenum to enable a LOM, which is in part responsible for the excellent OER performance obtained. These results were published in *Journal of Materials Chemistry A* in 2021.

In Chapter 3, I detail my work on the $\text{CoFe}_x\text{O}_y\text{-SO}_4$ system. Cobalt-iron oxide nanosheets containing SO_4^{2-} anionic groups were produced from the etching and partial cation exchange of cobalt-based ZIF-67 with an ammonium iron sulfate. The salt breaks

the polyhedral structure of ZIF-67, yielding porous assemblies of nanosheets, containing controlled amounts of iron and sulfate ions. The material composition and crystal structure can be adjusted to optimize its OER performance. The excellent performance is associated with the presence of the three elements, cobalt, iron and sulfate ions, and to the porous and amorphous structure of the material. In situ Raman spectroscopy analysis correlated with XPS data probes the material to be further oxidized to an oxohydroxide phase. It is further demonstrated here, that $\text{CoFe}_x\text{O}_y\text{-SO}_4$ samples catalyse the OER through an effective LOM mechanism. This work has been submitted for publication in 2022.

In Chapter 4, I detail the engineering of ultrathin CoMoP nanosheets using the Co-MOF ZIF-67 as a self-sacrificial template and ammonium molybdate as a shape-defining agent and Mo source. CoMoP nanosheets exhibit outstanding performance towards HER and OER in alkaline media, which I associate with the proper transport properties and electronic energy levels provided by their composition and their porous nanosheet structure. This work provides a suitable strategy to synthesize high-performance Co-Mo-P electrocatalysts with abundant exposed active sites and effective avenues for charge and electrolyte transport, and it can be employed to further tune the structure and composition of other 2D nanostructures with optimized performance towards OWS and other electrocatalytic reactions. This work has been accepted in *Nanomaterials* in 2022.

In Chapter 5, I detail a solution-based method developed to produce $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$ NPs with tuned metal ratios. The electrochemical performance of the materials was tested in 1 M KOH and 1 M KOH + 1 M ethanol aqueous electrolytes. CoSe_2 showed enhanced OER activity and NiSe_2 demonstrated a more efficient EOR. The incorporation of small amounts of Co to the NiSe_2 structure resulted in the highest EOR activities. DFT calculations showed that the presence of Co improved ethanol adsorption and decreased the barrier for ethanol dehydrogenation. This work provides a cost-effective approach to the high Faradaic efficiency electrochemical reforming of ethanol with acetate co-production. This work is also an excellent example for other small molecules oxidation and conversion into valuable chemicals. The results have been published in *Chemical Engineering Journal* in 2022.

Finally, the main conclusion of this thesis and some perspectives for future work are presented at the end of this thesis.

Resumen de Resultados

Los nanomateriales a base de cobalto son una clase importante de electrocatalizadores que poseen estructuras electrónicas orbitales abundantes y diversas y exhiben una excelente actividad catalítica para las reacciones de evolución de hidrogeno y oxígeno y la oxidación del etanol (HER, OER, EOR), y una gran estabilidad en la conversión de energía. A pesar de que algunos catalizadores de cobalto elemental, se han reconocido como candidatos potenciales para ciertas reacciones, el rendimiento cobalto elemental está lejos del resultado ideal. Para optimizar este catalizador, se desarrollaron materiales compuestos basados en cobalto mediante la introducción de otro elemento para aumentar área y conductividad eléctrica y para ajustar la estructura electrónica del material basado en cobalto. En esta tesis, detallo la producción y optimización de cuatro nanocatalizadores a base de cobalto, MoCo_xO_y , $\text{CoFe}_x\text{O}_y\text{-SO}_4$, CoMoP y $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$, para tres procesos clave de conversión de energía electroquímica, a saber, la evolución electroquímica del oxígeno, la generación de hidrogeno a partir de agua y la generación de hidrogeno a partir de la oxidación del etanol.

En el primer Capítulo, se presenta una introducción general sobre las tecnologías de conversión de energía electroquímica relevantes y los nanocatalizadores basados en cobalto para explicar la motivación de esta tesis.

En el segundo Capítulo detallo el caso de nanoláminas ultrafinas de MoCo_xO_y amorfas con un excelente rendimiento catalítico OER producidas mediante una estrategia asistida etching iónico y pirólisis. La incorporación de iones de molibdato no solo modifica la arquitectura del material para generar estructuras de nanoláminas en capas bidimensionales, sino que también regula el entorno de coordinación local y la estructura electrónica del óxido de cobalto. La incorporación de molibdeno introduce abundantes vacantes y especies adsorbidas de oxígeno. Además, la arquitectura amorfa de nanoláminas del material favorece la presencia de defectos en la superficie y sitios coordinativamente insaturados, lo que aumenta la exposición de los sitios activos y mejora aún más la actividad catalítica. Finalmente, varias evidencias experimentales revelaron la incorporación de molibdeno para habilitar un LOM, que es en parte responsable del excelente rendimiento de OER obtenido. Estos resultados se publicaron en *Journal of Materials Chemistry A* en 2021.

En el Capítulo 3 detallo la producción de nanoláminas de óxido de hierro y cobalto que contienen grupos aniónicos SO_4 a partir del etching y el intercambio catiónico parcial de ZIF-67 a base de cobalto con un sulfato de hierro y amonio. Se muestra cómo la sal rompe la estructura poliédrica de ZIF-67, produciendo ensamblajes porosos de nanoláminas, que contienen cantidades controladas de iones de hierro y sulfato. La composición del material y la estructura del cristal se pueden ajustar para optimizar su rendimiento OER. El excelente comportamiento está asociado a la presencia de los tres elementos, iones cobalto, hierro y sulfato, y a la estructura porosa y amorfa del material. El análisis de espectroscopia Raman *in situ* correlacionado con los datos de XPS prueba que el material se oxidará aún más a una fase de oxohidróxido. Aquí se demuestra además que las muestras de $\text{CoFe}_x\text{O}_y\text{-SO}_4$ catalizan la OER a través de un mecanismo LOM efectivo. Este trabajo había sido enviado para su publicación en 2022.

El Capítulo 4 detallo la producción de nanoláminas CoMoP ultrafinas utilizando el Co-MOF ZIF-67 como plantilla autosacrificada y molibdato de amonio como agente que define la forma y como fuente de Mo. Las nanoláminas de CoMoP exhibieron un rendimiento sobresaliente frente a HER y OER en medios alcalinos, lo que asociamos con las propiedades de transporte adecuadas y los niveles de energía electrónica proporcionados por su composición y su estructura porosa. Este trabajo proporciona una estrategia adecuada para sintetizar electrocatalizadores Co-Mo-P de alto rendimiento con abundantes sitios activos expuestos y vías efectivas para el transporte de carga y electrolitos, y puede emplearse para ajustar aún más la estructura y composición de otras nanoestructuras 2D con un rendimiento optimizado, hacia OWS y otras reacciones electrocatalíticas. Este trabajo ha sido aceptado en *Nanomaterials* en 2022.

En el Capítulo 5, detallo un método basado en solución para producir nanopartículas de $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$ con proporciones de metal controladas. El rendimiento electroquímico de los materiales se probó en electrolitos acuosos de KOH 1 M y KOH 1 M + etanol 1 M. CoSe_2 mostró una actividad OER mejorada y NiSe_2 demostró una EOR más eficiente. La incorporación de pequeñas cantidades de Co a la estructura de NiSe_2 resultó en las actividades de EOR más altas. Los cálculos de DFT mostraron que la presencia de Co mejoró la adsorción de etanol y disminuyó la barrera para la deshidrogenación de etanol. Este trabajo proporciona un enfoque rentable para el reformado electroquímico de etanol con coproducción de acetato de alta eficiencia Faradaica. Este trabajo también es un excelente ejemplo para la oxidación y conversión de otras moléculas pequeñas en

sustancias químicas valiosas. Los resultados se han publicado en *Chemical Engineering Journal* en 2022.

Finalmente, la conclusión principal de esta tesis y algunas perspectivas para el trabajo futuro se presentan al final de esta tesis.

List of Acronyms

OWS	Overall water splitting
HER	Hydrogen evolution reaction
OER	Oxygen evolution reaction
MOR	Methanol oxidation reaction
EOR	Ethanol evolution reaction
DLFCs	Direct liquid fuel cell
XRD	X-ray diffraction
AFM	Atomic force microscopy
CV	Cyclic voltammetry
EDS	Energy dispersive spectroscopy
BET	Brunauer–Emmett–Teller
BJH	Barrett–Joyner–Halenda
EELS	Electron energy loss spectroscopy
EIS	Electrochemical impedance spectroscopy
FTIR	Fourier transform infrared
HRTEM	High-resolution transmission electron microscopy
HAADF	High angle annular dark-field
C _{dl}	Double-layer capacitance
HAADF-STEM	Annular dark-field scanning transmission electron microscope
RHE	Reversible hydrogen electrode
SEM	Scanning electron microscope
TGA	Thermogravimetric analyses
XPS	X-ray photoelectron spectroscopy
ICP-MS	Inductively coupled plasma- mass spectrometry
ZIF-67	Zeolitic imidazolate framework

MOFs	Metal-organic frameworks
AEM	Adsorbate evolution mechanism
LOM	Lattice oxygen oxidation mechanism
FFT	Fast Fourier transform
GC	Gas chromatography
CA	Chronoamperometry
IC	Ion chromatography
NPs	Nanoparticles
BEs	Binding energies
ECSA	Electrochemical active area
VASP	Vienna ab initio package
DFT	Density functional theory
GGA	Generalized gradient approximation
PAW	Projected augmented wave

Chapter 1

General Introduction

1.1 Renewable Energy

Energy is closely related to the development and progress of human society. Especially since entering the new century, it has become an important factor restricting human development. The world's energy consumption is expected to peak between 2030 and 2040, with total consumption about twice the current level.^{1,2} At present, the combustion of fossil fuels is still the main way we obtain energy. However, the non-renewability of fossil fuels and the pollution caused by their combustion have also caused a huge negative impact on human economic development and the ecological environment.³ We are currently facing serious energy problems and environmental crises. Thus, actively looking for efficient, clean and sustainable alternative energy sources is the only way out from the present situation. At present, wind energy, hydropower, solar energy and tidal energy, which are economical, clean, safe and efficient renewable energy sources that can replace fossil fuels, have been widely developed.⁴ However, these clean energy sources are unstable and intermittent, which seriously restricts their deployment. Hydrogen obtained by water electrolysis and biomass-derived products like methanol and ethanol are extremely interesting energy carriers due to their high energy density (142 MJ kg⁻¹ for hydrogen, 27 MJ kg⁻¹ for ethanol), sustainability, and potential environmentally friendly production and conversion.⁵⁻⁸

1.2 Energy Conversion Technology

Converting electrical energy into chemical energy by electrochemical means is considered a feasible strategy to store electricity to be afterwards recovered using fuel cells. Electrochemical energy storage and conversion systems can be a sustainable and environmentally friendly solution to the current energy crisis.^{9, 10} Among them, the electrolytic cell can directly convert electrical energy into chemical hydrogen energy.¹¹ The production of hydrogen by water splitting has the following advantages: firstly, it relies on an interfacial chemical reaction, which can allow energy conversion with high thermodynamic and theoretical efficiency; secondly, it allows storing electricity into

chemical energy at any time and location, since water is an abundant resource; finally, and most importantly, the combustion of hydrogen eventually only produces water, which almost no impact on the environment. Besides, the produced water can be electrolyzed to produce hydrogen again, so it is a recyclable and pollution-free energy conversion process. These advantages make it considered as one of the most potential energy technologies in the future.^{12, 13}

Direct fuel cells are portable power generation devices that convert chemical energy into electrical energy with high efficiency and environmental friendliness through an electrode-electrolyte system. They are considered to be one of the most promising sustainable energy conversion technologies.^{14, 15} Compared with traditional combustion and power generation technologies, and also batteries, fuel cells have many advantages, such as no need for a long charging process, both fuel and oxidant can be supplied from the outside of the device, high energy conversion efficiency, and most importantly, the fuel cell produces only CO₂ and H₂O, could effectively reduce NO_x, SO₂ and particulate matter emissions.¹⁶ Direct alcohol fuel cells that replace fossil fuel with liquid fuels such as methanol and ethanol have attracted more and more attention due to the abundant sources of liquid fuels, easy storage and transportation, and high energy density.^{17, 18}

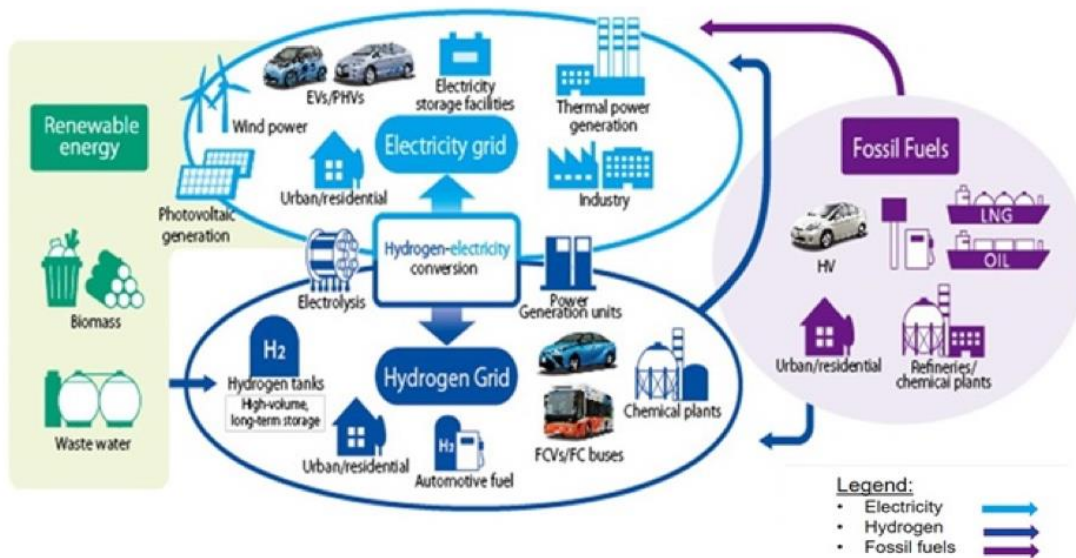


Figure 1.1 Toyota's vision of the hydrogen economy.¹⁹

1.2.1 Electrochemical water splitting

Electrochemical water splitting includes two half-reactions: reduction reaction of H⁺ to generate H₂ (hydrogen evolution reaction, HER) on the cathode and the oxidation reaction

of O^{2+} that occurs in the anode to generate O_2 (oxygen evolution reaction, OER) of an electrolyte cell.^{20, 21} A typical electrolytic cell (Figure 1.2) setup consists of the following parts: an external power supply; an electrolyte solution; and two electrodes that are connected to the external power supply and form a loop. The anode electrode in the electrolytic cell device is connected with the positive electrode of the external power supply, and the cathode electrode is connected with the negative electrode of the external power supply. During the working process (taking the electrolysis of water to produce hydrogen and oxygen as an example), the electrons flow from the negative electrode of the external power supply – the cathode of the electrolytic cell – to the anode of the external power supply – the positive electrode of the external power supply, and the current flow is just the opposite.²²

Under standard conditions (25 °C and 1 atm), the theoretical thermodynamic potential for water splitting is 1.23 V regardless of the electrolyte (acidic or alkaline). Practically, a much higher voltage than the theoretical value (the difference is called overpotential) is required to drive water splitting at a satisfying reaction rate. The overpotential (η) comes from the activation barrier of anode and cathode as well as other resistance (e.g., contact and solution resistances). The practical potential (EP) for water splitting can be then expressed as

$$E_p = 1.23 \text{ V} + \eta_a + \eta_c + \eta_{\text{other}}$$

where η_a , η_c and η_{other} denote the partial overpotential from the anode, cathode and other resistance, respectively. Highly efficient electrocatalysts have to be adopted to decrease the overpotential coming from the anode and cathode sides.

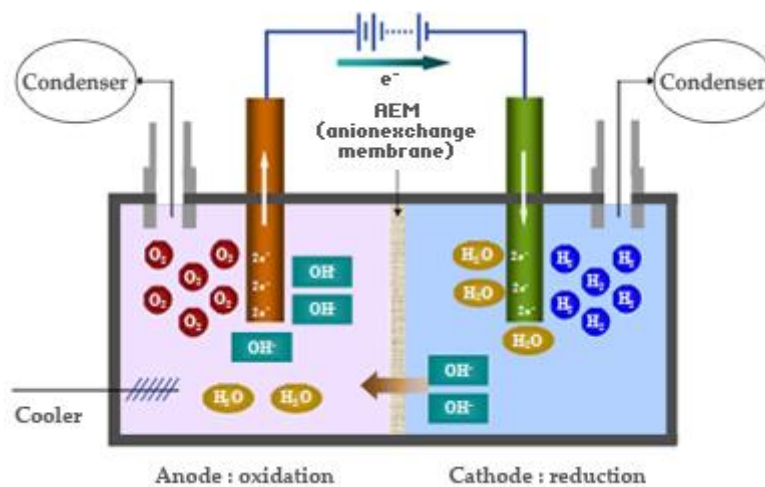
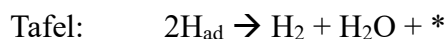
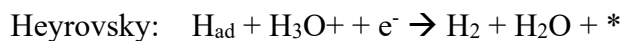
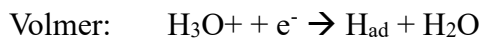


Figure 1.2. Schematic diagram of an electrolyzer.²²

1.2.2 Hydrogen Evolution Reaction (HER)

The hydrogen evolution reaction process can be described by the following three reaction steps



Among them, H_{ad} represents the surface-bonded H atom; * represents the hydrogen adsorption site. The hydrogen evolution reaction (HER) can occur via the Volmer-Heyrovsky pathway or the Volmer-Tafel pathway (as shown in Figure 1.5).²³ During the hydrogen evolution reaction, H atoms are adsorbed on the catalyst surface through the Volmer reaction. Then H_2 is released from the interface through the Tafel reaction.²⁴ If the kinetics of the desorption process is slow at room temperature, the Volmer reaction is the rate-determining step of the hydrogen evolution reaction, and the Tafel slope at this time is 118 mV dec^{-1} .²⁵ If the desorption process rate is fast enough at room temperature, the Heyrovsky reaction or the Tafel reaction is the rate-determining step of the hydrogen evolution reaction, and the Tafel slopes at this time are 39 mV dec^{-1} and 29.5 mV dec^{-1} , respectively.²⁶ The small Tafel slope means that the current density of the hydrogen evolution reaction increases rapidly with increasing overpotential. Therefore, hydrogen evolution reactions involving the Heyrovsky reaction or the Tafel reaction as the rate-determining step are advantageous.²⁷ The key to the above three reactions is to form a bonded H_{ad} on the electrode surface. The bonding force between H_{ad} and the electrode should not be too strong (too strong will inhibit the Volmer reaction) nor too weak (too weak will inhibit the Heyrovsky reaction or the Tafel reaction).²⁸ The hydrogen evolution catalyst volcano diagram is a good example of the relationship between the hydrogen evolution activity of the catalyst and the free energy of hydrogen binding (as shown in Figure 1.3a).

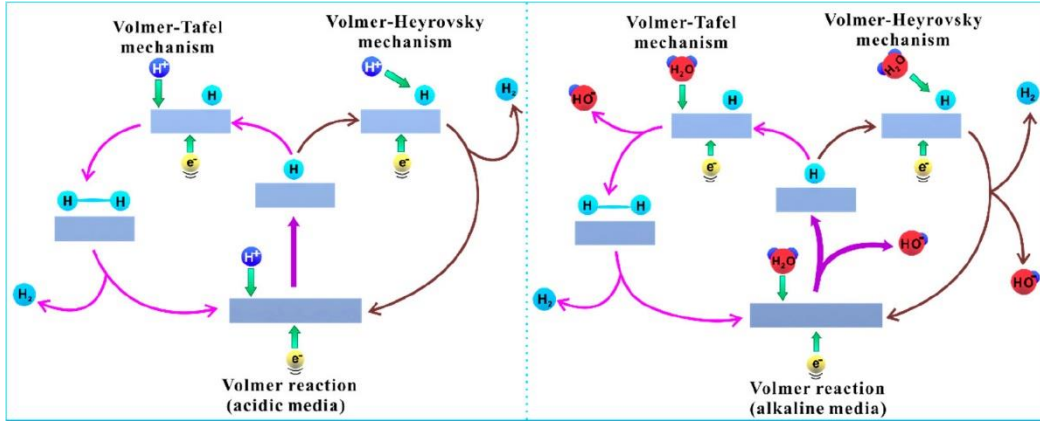


Figure 1.3. Mechanism of hydrogen evolution on the surface of an electrode in acidic (left) and alkaline (right) solutions.²³

1.2.3 Oxygen Evolution Reaction (OER)

As a half-reaction of electricity-driven water splitting, the oxygen evolution reaction (OER) is the major bottleneck due to the sluggish kinetics of this four-electron transfer reaction.²⁹ It is widely accepted that OER can proceed through two different mechanisms: conventional adsorbate evolution mechanism (AEM) and lattice-oxygen-mediated mechanism (LOM).³⁰

The AEM is typically assumed to involve four concerted proton–electron transfer (CPET) reactions centered on the metal ion, as described in eqn (1) – (4). At each step, a proton is injected into the electrolyte, eventually combining with a transferred electron at the cathode. In particular, OH^- first adsorbs on the surface O vacancy site (eqn (1)). The adsorbed OH (HO^* species) then undergoes subsequent deprotonation to form O^* (eqn (2)). The following O–O bond formation step allows O^* to react with another OH^- to form the HOO^* intermediate (eqn (3)). In the final step, O_2 is evolved through the deprotonation of HOO^* with the regeneration of the active site (eqn (4)).^{30, 31}



LOM proceeds on two neighboring metal sites, which is different from that in conventional AEM that proceeds on a single metal site. Firstly, two HO^* on the metal sites undergo deprotonation, resulting in two metal–oxo species. Secondly, these two neighboring oxo species directly couple to form the O–O bond instead of combining with

water or OH^- to form HOO^* . Finally, O_2 is released with the bareness of two vacant metal centers that are subsequently occupied by OH^- . Because HOO^* is not an intermediate in the LOM catalytic cycle, water oxidation after LOM becomes independent of the limitation (minimal overpotential of about 0.37 V) of the scaling relation between HO^* and HOO^* . In the past few decades, a heterogeneous water oxidation catalyst has not been used for conducting LOM to form O_2 by direct O–O coupling, because this process is considered to need a large activation barrier. In fact, this process has been widely accepted to operate in certain molecular catalysts involving transition metals. In this part, we introduce the significant progress made in LOM for OER in recent years as well as catalyst design methods.^{32, 33}

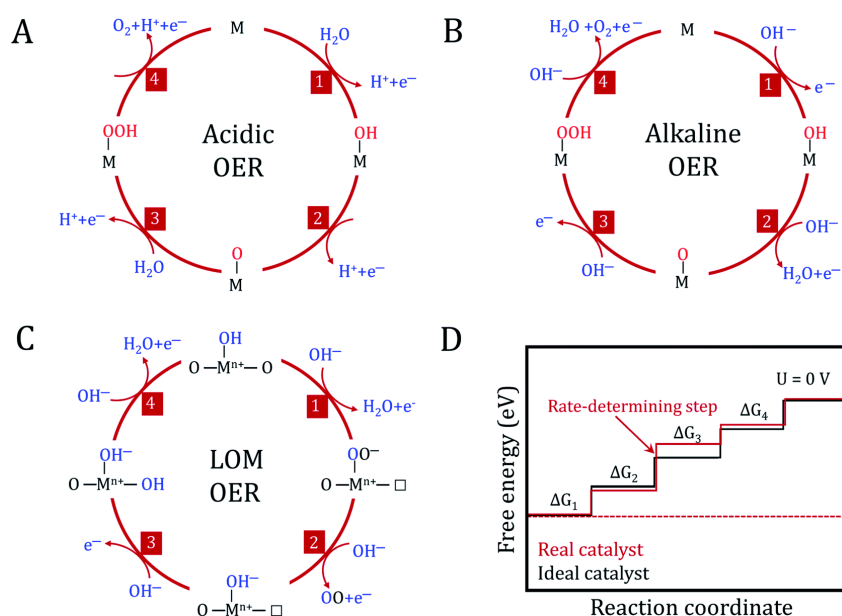


Figure 1.4. The oxygen evolution reaction mechanism. Conventional OER mechanism for acidic (A) and alkaline (B) conditions. (C) Reaction mechanism for the OER, including the participation of lattice oxygen in an alkaline environment. M represents the active site and $\square$ represents the oxygen vacancy. (D) Plot of the Gibbs free energy of reactive species and intermediates (horizontal lines) of the OER versus the reaction coordinates. The blue and red lines indicate the energetics of a real and ideal catalyst, respectively. The dashed lines indicate the energetics at the electrode potential where all of the thermochemical barriers disappear.³⁴

1.2.3 Direct liquid fuel cells (DLFCs)

Direct liquid fuel cells (DLFCs), which directly use liquid fuels like methanol, ethanol, formic acid, etc. as fuel, have received increasing attention in the past 10 years.³⁵ They are convenient, fast and provide high volumetric energy density. In addition, these liquid fuels are also very easy to store, transport and replenish.³⁶ DLFCs can offer up to 10 times

the energy density of rechargeable batteries and operate at ambient temperatures, which significantly reduces thermal management of the system.³⁷ These advantages make the technology very attractive to the rapidly growing demand for portable power supplies ranging from sub-watts to hundreds of watts.³⁸ In DLFCs, a liquid fuel is fed directly to the anode, at which an oxidation reaction occurs, while air or oxygen gas is sent to the cathode for the reduction reaction.³⁹ The charged ions pass through the electrolyte, and electrons travel via an external circuit. There will always be some side product produced in the anode due to incomplete oxidation of fuel, whereas, at the cathode, the waste product will be mostly water.⁴⁰ Figure 1.5 shows a diagram outlining the general operation of DLFCs.

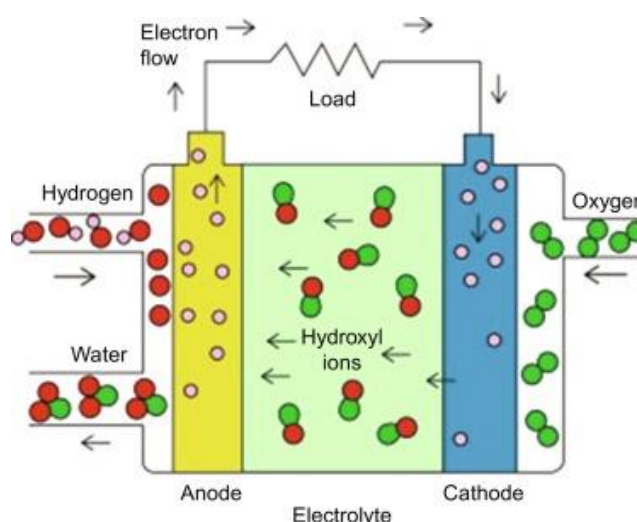


Figure 1.5. Schematic diagram of DLFCs.⁴¹

1.2.3 Methanol oxidation reaction (MOR)

Alcohol oxidation is a process involving multiple steps of adsorption and dissociation. First, methanol molecules are adsorbed on the surface of the catalyst to form adsorbed methanol molecules.^{42, 43} Under the action of the catalyst, the C-H bonds of the adsorbed methanol molecules begin to activate to generate intermediate products such as CO, which are finally oxidized to CO₂ under high voltage.^{44, 45} However, the generated CO intermediate products will be adsorbed on the surface of the catalyst, especially the strong interaction between CO and platinum group catalysts, which will cause the catalyst to lose its activity rapidly during the reaction process (Figure 1.6).⁴⁶

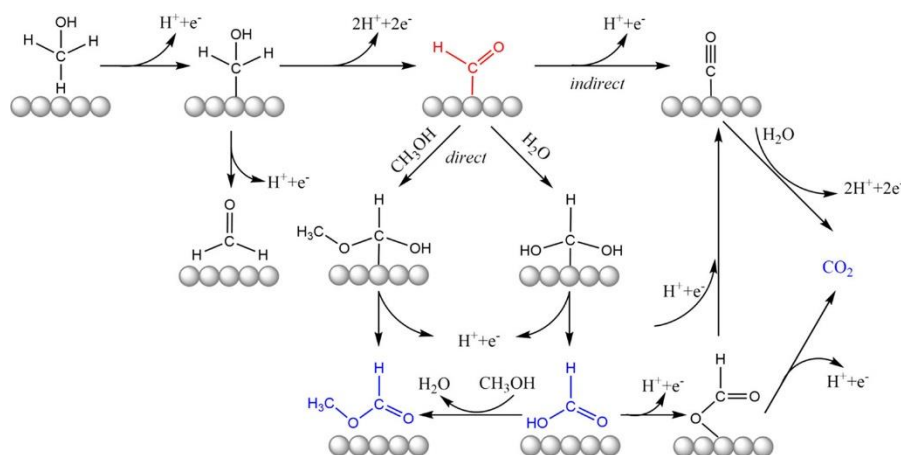


Figure 1.6. Proposed reaction mechanism for methanol oxidation. The adsorbed HCO species determines whether the reaction proceeds via the indirect or direct pathway.⁴⁶

1.2.4 Ethanol oxidation reaction (EOR)

Ethanol oxidation reaction is a 12-electron transfer process.^{47, 48} There are two main pathways for this reaction. The process of ethanol generating products such as acetaldehyde or acetic acid through 2 electrons or 4 electrons process is the C2 pathway.^{49, 50} In this reaction pathway, ethanol is not completely oxidized, and most of the energy remains in products such as acetaldehyde and acetic acid, resulting in severe energy loss.⁵¹ The complete oxidation of ethanol to CO₂ is the C1 pathway, which involves C-C cleavage to form intermediate products such as CO, which is oxidized to CO₂ at high potentials.⁵² However, the generated intermediate product CO is often adsorbed on the surface of the catalyst, causing the catalyst to lose its activity.⁵³ Figure 1.7 below is a schematic diagram of the C1 and C2 pathways for the oxidation of ethanol to CO₂, acetaldehyde, and acetic acid.⁵³

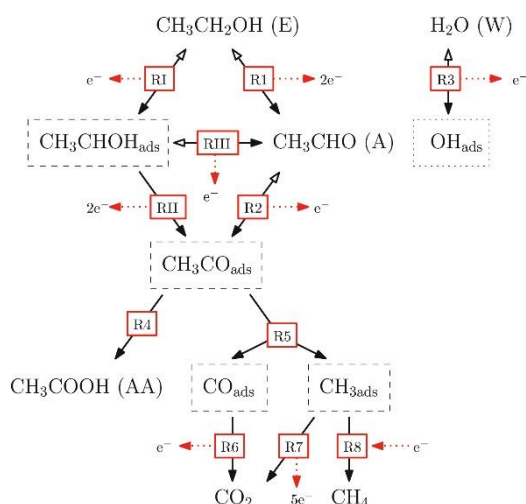


Figure 1.7. Reaction mechanism for the ethanol oxidation reaction (EOR) on binary Pt-based catalysts proposed in this work. Pt-site adsorbed species are indicated by a dashed box; OH_{ads} is boxed using dotted lines to indicate that it is adsorbed on the secondary metal sites.⁵³

1.3 Cobalt-based nanocatalysts

Whether it is electrocatalytic water splitting or direct liquid fuel cells, highly efficient catalysts are required to drive these reactions. Platinum-based noble metal materials (Pt, Ir, Ru, Rh, Pd) are the best electrocatalysts for HER, OER, and EOR with extremely high catalytic activity.^{54, 55} However, due to rare earth reserves, low natural abundance and high cost, the large-scale commercial application is seriously restricted.⁵⁶ Therefore, they are not ideal industrial catalysts. Developing highly efficient, low-cost, resource-abundant electrocatalysts remain a challenge. First transition metals such as Ni, Co, Mn, and Fe have attracted extensive attention due to their high abundance and relatively good electrocatalytic activity.⁵⁷⁻⁵⁹ Especially for cobalt-based nanocatalysts, abundant and diverse d-orbital electronic structures, enable good HER, OER, EOR catalytic activity and stability. A series of cobalt-based catalytic center materials such as carbides,⁶⁰ borides,^{61, 62} oxides/hydroxides,⁶³⁻⁶⁷ phosphides,⁶⁸ chalcogenides,⁶⁹⁻⁷¹ alloys⁷² and single atoms,⁷³ have been recognized as potential candidates. However, the performance of the alone cobalt catalyst is far from the ideal result. Some composite cobalt-based nanocatalysts have been developed by introducing other transition metals such as Zn,^{74, 75} Ni,^{76, 77} Mn,^{78, 79} Fe,^{80, 81} Cu,^{82, 83} Mo^{84, 85} etc. Due to the introduction of the second transition metal, the d-band center of the cobalt is adjusted, the adsorption energy and activation energy of the reaction are reduced, and the catalytic performance and stability of the nanocatalyst are greatly improved.⁸⁶ They can provide parallel or even better activities, and superior electrochemical stability, compared with precious metals materials.⁸⁷

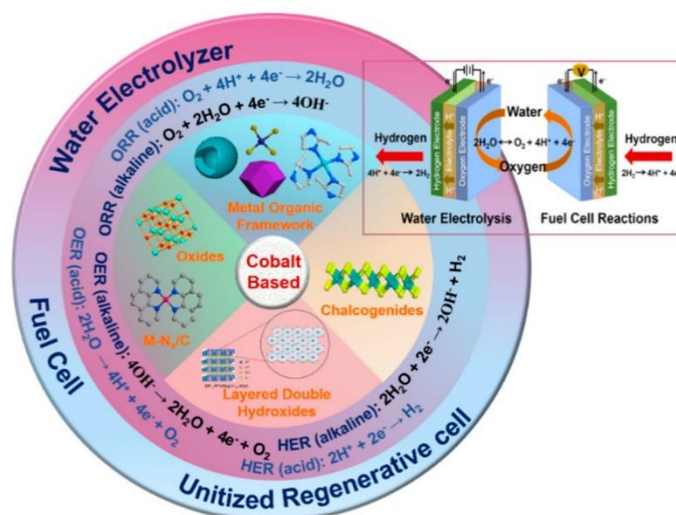


Figure 1.8. application of cobalt-based nanocatalysts in energy conversion.⁸⁸

1.4 Synthesis of cobalt-based nanocatalysts

To date, a variety of methods have been developed to prepare cobalt-based nanocatalysts, including ion exchange,^{89, 90} calcination,^{91, 92} hydrothermal,^{93, 94} electrochemical deposition,⁹⁵ gas-phase reaction,⁹⁶ colloidal synthesis,^{97, 98} ball milling method⁹⁹ etc. Among these the ion exchange method and colloidal synthesis will be mainly applied to produce nanostructured cobalt-based catalysts involved in this thesis, and thus will be detailed in the following text.

1.4.1 ion exchange

Ion exchange was utilizing the reversible exchange of an ion in the insoluble solid with another ion in its surrounding solution, which was originally technology used to soften water, demineralize, purify chemicals and separate substances. In recent years, it has been used to synthesize composite multicomponent hollow nanomaterials by using some single-component structured nanotemplate materials, such as MOFs,^{100, 101} nanocrystals,^{102, 103} etc. As for the case of nanocrystals, Figure 1.9 shows the synthetically feasible pathways to 65,520 distinct multicomponent metal sulfide nanorods having as many as 6 materials, 8 segments, and 11 internal interfaces by applying up to seven sequential cation-exchange reactions to copper sulfide nanorod precursors.¹⁰⁴

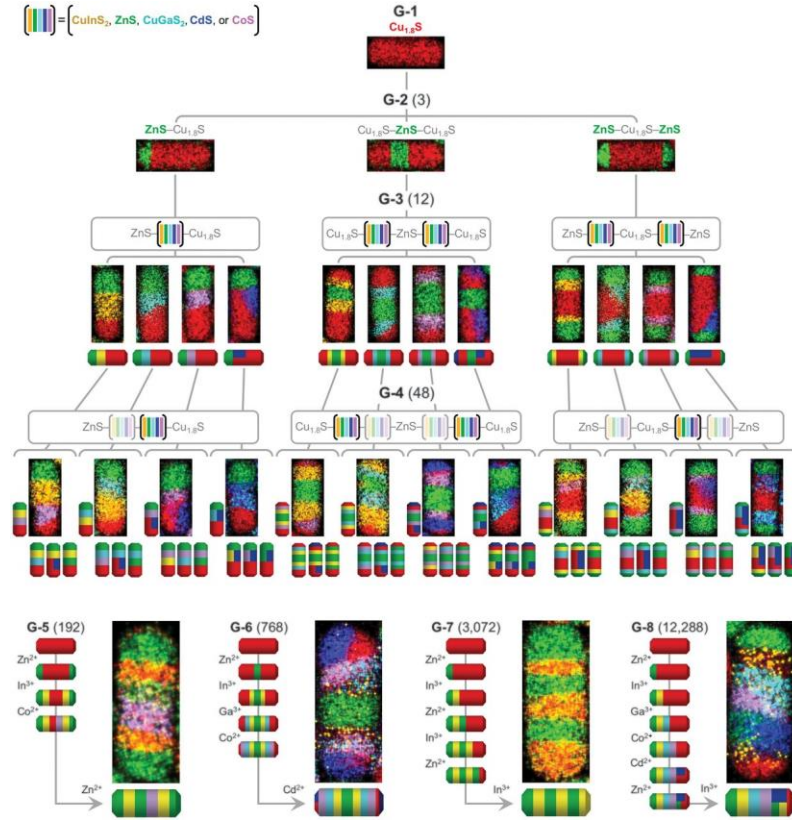


Figure 1.9. Synthetic pathways to 16,380 distinct G-3 through G-8 nanorods.¹⁰⁴

Metal-organic frameworks (MOFs) are a new crystalline material with ordered spatial topological structure.¹⁰⁵ Therefore, it could be used as the template for the design and synthesis of high-performance hollow nanostructured catalysis. Due to the stable carbon framework of MOFs, the derived materials obtained by ion exchange have rich components, large specific surface area and abundant catalytically active sites.^{106, 107}

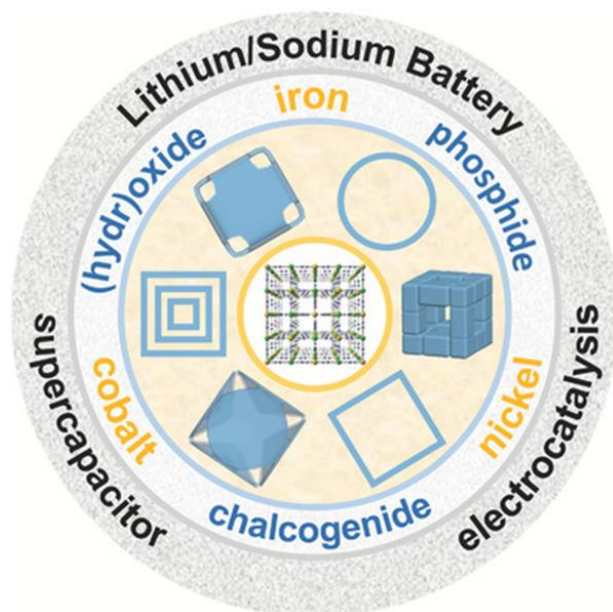


Figure 1.10. Hollow Structures Based on MOFs for Electrochemical Energy Storage and Conversion.¹⁰⁸

1.4.2 Colloidal synthesis

Colloidal synthesis routes allow producing nanocrystals materials with high level of control over the size, shape and composition.¹⁰⁹ As such, the use of metal colloids as a component of catalyst design has gained increasing attention for the controlled creation of catalysts with the appropriate level of complexity.^{110, 111} A typical chemical reduction-based synthesis (Figure 1.11) entails the dissolution of precursors of the desired metal into a solvent in the presence of a protective agent.¹¹² In the following step, the reduction process proceeds at elevated temperature to generate metallic NPs by introducing a reducing agent. In the case of protocols based on thermal decomposition, two common approaches are applied. The first, represented in Figure 1.11b, is near-identical to the chemical reduction approach described above; it only differs in the fact that no reducing agent is applied at elevated temperature and that this temperature is mostly higher than in the case of chemical reduction methods, e.g. ~ 200 °C versus ~ 100 °C. Another protocol relies on “hot injection” of the metal precursor (Figure 1.11c). Herein, solely the solvent and protective agent are first added to a reaction vessel. After heating this mixture, the precursor – typically dissolved in the same solvent as present in the reaction vessel – is injected into the ‘hot’ reaction mixture. After a certain dwell time at the final temperature, the synthesis is terminated by cooling off the system.

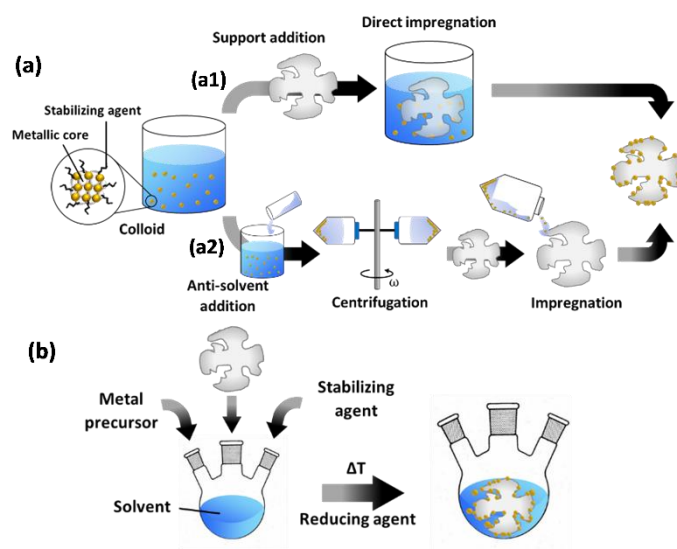


Figure 1.11. Common protocols for colloid synthesis: (a) chemical reduction; (b) thermal decomposition with precursor added in the initial step; (c) thermal decomposition via hot injection. The blue-green content of the syringe indicates that the metal precursor (green) is dissolved in the same solvent as the reaction vessel (blue).¹¹²

1.5 Challenges

Cobalt-based nanocatalysts have been widely investigated by researchers due to their generous earth reserves and high activity. However, the investigations of cobalt-based nanocatalysts for energy conversion are still at the proof-of-concept level. there are still some great challenges in energy conversion, as detailed separately below:

- 1) To meet the actual demand for the industry, economical and scalable synthetic methods should be further developed to prepare cobalt-based nanocatalysts with high activity and durability.¹¹³
- 2) From the aspect of structural design, in-depth understandings of the basic material science and chemical reaction mechanism are still required to identify the complex effects (strain effect, ensemble effect, synergistic effect, etc.) on the underlying origins for electrochemical energy conversion reaction.^{114, 115}
- 3) The role of temporal–spatial ordering in mass transfer, storage, and release in the cobalt-based nanocatalysts should be further investigated based on theoretical calculations and experimental data to optimize these unique nanoreactors.¹¹⁶
- 4) From the performance point of view, *in situ/operando* high-resolution characterizations are needed to study the reason of performance degradation for practical

utilization of cobalt-based nanocatalysts in electrolyzed water splitting and direct fuel cell.^{117, 118}

5) Although the catalytic mechanisms for water splitting including HER and OER and direct fuel cells including MOR and EOR have been proposed, the detailed mechanisms, especially at the atomic level, are still ambiguous and require more in-depth investigation.^{119, 120}

1.6 Objectives

Taking all the aspects mentioned above, the goal of this thesis is to develop highly efficient cobalt-based nanocatalysts for electrochemical energy conversion, and to explore and study the catalytic reaction mechanisms. Keeping these aims in mind, several specific objectives are defined as follows:

- 1) To explore the formation of amorphous ultrathin MoCo_xO_y nanosheets through an ion etching and pyrolysis assisted strategy used MOFs as templates. Meanwhile, to explore the reaction mechanism during OER process by *in situ* Raman technology.
- 2) To demonstrate the effect of sulfate anion groups adsorbed on the catalyst surface on OER performance. Simultaneously, to reveal the reaction pathway of $\text{CoFe}_x\text{O}_y\text{-SO}_4$ in OER process using *in situ* Raman.
- 3) To optimize bifunctional nanocatalysts for electrocatalytic water splitting. The obtained electrocatalysts should own excellent OER and HER performance to be used as anode and cathode material for overall water splitting.
- 4) To develop a solution-based method to produce $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$ NPs with tuned metal ratios and test if for EOR.

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Chapter 2

Activating the lattice oxygen oxidation mechanism in amorphous molybdenum cobalt oxide nanosheets for water oxidation

2.1 Abstract

The cost-effective deployment of several key energy technologies, such as water electrolysis, CO₂ electroreduction and metal-air batteries, relies on the design and engineering of cost-effective catalysts able to accelerate the sluggish kinetics of the oxygen evolution reaction (OER). Herein, we detail the synthesis, processing and performance of a cobalt oxide-based OER electrocatalyst with optimized composition, atomic arrangement and nano/microstructure. We demonstrate that doping the cobalt oxide with a higher electronegativity element such as molybdenum promotes the participation of lattice oxygen in the OER reaction. Besides, the processing of the catalyst at moderate temperatures results in an amorphous material with extended compositional and atomic arrangement versatility. Additionally, the catalyst, which is produced through an ion etching assisted strategy using ZIF-67 as a template, displays a highly porous structure in the form of amorphous ultrathin MoCo_xO_y nanosheets that maximize interaction with the media and facilitate the transport of ions through the electrolyte.

2.2 Introduction

The energy efficiency of several key energy processes and technologies, including water electrolysis, nitrogen and CO₂ reduction, regenerative fuel cells and rechargeable metal-air batteries, is in large part limited by the sluggish kinetics of the oxygen evolution reaction (OER).¹⁻⁴ On top of the moderate efficiencies, current best OER catalysts are based on high cost and rare elements, such as IrO₂ and RuO₂, which further limits the cost-effectiveness of these technologies.⁵ To overcome these limitations, high activity OER electrocatalysts based on abundant transition metals need to be developed.⁶⁻⁸

In most electrocatalysts, OER proceeds through the adsorbate evolution mechanism (AEM).⁹⁻¹¹ This conventional mechanism requires catalysts with proper adsorption sites,

i.e. surface sites that, according to the Sabatier principle, bind reactants/intermediates/products neither too strongly nor too weakly.¹²⁻¹³ Recently, several works have evidenced that some OER oxide catalysts are particularly active due to the participation of lattice oxygen in the reaction.¹⁴⁻¹⁶ In this lattice oxygen oxidation mechanism (LOM), the catalyst performance does not rely on how close to the top of a volcano-like trend their surface adsorption sites lay, but on the covalence of the metal-oxygen bonds and the suitability of the catalyst surface but also bulk electronic structure. These parameters can be tuned by adjusting the catalyst bulk composition, introducing vacancies or extrinsic metal dopants.¹⁷⁻²⁰ More specifically, LOM can be particularly promoted through doping with high electronegative cations that facilitate the participation of lattice oxygen in the reaction.²¹

Transition metal oxides (TMOs) have been widely explored as promising electrocatalysts for OER in alkaline medium ($4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$).²²⁻²⁵ Within a LOM mechanism, to optimize the OER performance of a catalyst, the oxygen p band needs to be shifted close to the Fermi level to trigger the redox activity of the lattice oxygen. This requires strong metal d- and oxygen p-band overlap.²⁶ Cobalt-based oxides and particularly oxohydroxides are particularly interesting owing to their high thermal stability, abundance, suitable 3d electronic configuration, and potential layered structure that allows water penetration to interact with the whole material. The most effective strategy to increase the covalence of the cobalt oxide framework and promote LOM is to lower the energy of the transition metal d orbital by incorporating a more electronegative metal. Thus, an excellent candidate dopant to promote the OER activity of cobalt oxides is molybdenum.

Mo^{6+} is a high-valence 4d transition metal ion with a 0.62 Å ionic radius that matches well with that of Co^{3+} (0.63 Å). These similar sizes allow for Mo doping into CoO_x in the form of substituted Co^{3+} .²⁷⁻²⁹ Mo doping has been evidenced to improve the electrical conductivity and stability of different host materials.^{30,31} Besides, high valence metal ions and particularly Mo^{6+} can induce the targeted downshift of the host metal d-band to penetrate the p-band of adsorbed and lattice oxygen, sharing the ligand holes, making lattice oxygen atoms electrophilic, and thus more prone to participate in water oxidation.^{26,}

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In terms of atomic arrangement, amorphous catalysts are particularly advantageous within a LOM mechanism. Amorphous catalysts offer higher flexibility in terms of composition and atomic arrangement, which allows for more facile incorporation of a wide range of extrinsic dopants and concentrations.³⁶ A higher variety of oxidation states of multivalence metals is also possible in amorphous structures, which contain more unsaturated coordination spheres. Amorphous oxides are also generally characterized by less strongly bond oxygen ions compared with crystalline materials. Besides, the structural and compositional versatility of amorphous catalysis allows them to locally adapt their structure, i.e. atomic distribution and valences, under reduction and oxidation conditions/potentials, which also facilitates the participation of lattice oxygen in the reaction.³⁶ Beyond OER, amorphous catalysts frequently outperform crystalline materials in a variety of catalytic reactions and may require less demanding processing in terms of energy and time.³⁷ Besides, amorphous catalysts also contain abundant and varied defects that could provide adsorption/reaction sites for different species and additional activity.³⁶⁻⁴³ Amorphous materials may also contain a higher percentage of atoms exposed to the media and higher porosity, which allows a thorough diffusion of electrolyte to take advantage of the whole electrocatalytic layer. Indeed, amorphous catalysts generally display higher electrochemical surface areas (ECSA) when compared to crystalline materials.^{44,45} Their flexibility also allows an easier surface and volume reconstruction of active sites that translate into a self-healing ability and thus higher stability. As a drawback, the metal dissolution rate of amorphous materials is frequently higher, which reduces their stability, particularly under demanding operating conditions such as high currents. Additionally, the precise analysis of the catalytic mechanisms and their optimization are much more challenging owing to their much higher complexity.

Besides optimizing the composition and atomic arrangement, high activity catalysts require a maximized exposure with the media, and effective transport of electrolyte through the whole catalyst surface. In this direction, the use of ultrathin material architectures such as nanosheets is highly advantageous.⁴⁶⁻⁴⁸ Considering all the above requirements, herein, we detail the synthesis of Mo⁶⁺-doped CoO_x in the form of amorphous and ultrathin sheets from a metal-organic framework (MOF) using an ion etching-assisted strategy. We explore its performance toward OER, comparing it with that of a reference IrO₂ catalyst. The effect of Mo concentration and annealing time on

the OER overpotential, Tafel slope and stability is particularly analyzed. Finally, the reaction mechanism is discussed.

2.3 Experimental section

2.3.1 Chemicals

Ammonium molybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, 90%), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, 99.9%), potassium hydroxide (KOH, 85%), iridium(IV) oxide (IrO_2 , 99.9% metal basis), and Nafion (5 wt% in a mixture of low aliphatic alcohols and water) were obtained from Sigma-Aldrich. 2-Methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$, 99%) was purchased from Acros Organics. Methanol, ethanol and isopropanol were of analytical grade and obtained from various sources. Milli-Q water was obtained from a Purelab flex from Elga. All chemicals were used as received, without further purification.

2.3.2 Synthesis of zeolitic imidazolate framework (ZIF-67)

ZIF-67 was produced following a modified version of a previously reported procedure.^{49,50} Typically, 0.87 g $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ was dissolved in 30 mL methanol to obtain a clear solution. Subsequently, the solution was poured into 30 mL methanol containing 1.97 g 2-methylimidazole under vigorous stirring. After mixing completely, the solution was incubated for 24 h at room temperature. Purple precipitates were collected by centrifugation, washed with methanol at least three times, and finally dried at 60 °C overnight.

2.3.3 Synthesis of Mo-Co MOFs

120 mg of as-prepared ZIF-67 powder was ultrasonically dispersed in 20 mL ethanol. The dispersion was poured into a 100 mL aqueous solution containing 50 mg, 100 mg or 200 mg of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ under magnetic stirring. The mixture was then stirred vigorously for 12 hours at room temperature. Lavender-colored precipitates were collected by centrifugation, washed with water at least three times, and finally freeze-dried overnight. The obtained products were labelled as Mo-Co MOF-50, Mo-Co MOF-100 and Mo-Co MOF-200. The effect of stirring time was analyzed by preparing Mo-Co MOF-100 with different stirring times: 1 h, 3 h and 12 h. The effect of the Mo precursor was analyzed by replacing $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ with the equivalent molybdenum molar amount of $\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$, to obtain a sample labelled as Na_2MoO_4 -ZIF-67.

2.3.4 Synthesis of Co₃O₄ nanocrystals and amorphous MoCo_xO_y nanosheets

ZIF-67 and Mo-Co MOF powders were annealed in a muffle furnace at 350 °C for 2 h with a heating rate of 3 °C min⁻¹ under an air atmosphere. Black products were collected after natural cooling to ambient temperature and labelled as Co₃O₄ and MoCo_xO_y-50, MoCo_xO_y-100, MoCo_xO_y-200, and Na₂MoO₄-MoCo_xO_y, depending on the MOF precursor powder used. To explore the effect of the annealing temperature, the Mo-Co MOFs-100 was also annealed at 450 °C and 550 °C for 2 h. Table S1 lists all the samples produced and tested in this study.

Table S1. Complete list of samples produced and characterized, including name, precursors and processing conditions.

Sample name	MOF	Mo precursor	Mo precursor amount (mg)	Stirring time (h)	Annealing temperature (°C)
ZIF-67	ZIF-67	-	-	-	-
Mo-Co MOF-50	ZIF-67	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	50	12	-
Mo-Co MOF-100	ZIF-67	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	100	12	-
Mo-Co MOF-100-1h	ZIF-67	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	100	1	-
Mo-Co MOF-100-3h	ZIF-67	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	100	3	-
Mo-Co MOF-200	ZIF-67	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	200	12	-
Na ₂ MoO ₄ -ZIF-67	ZIF-67	Na ₂ MoO ₄ ·2H ₂ O	140	12	-
Co ₃ O ₄	ZIF-67	-	-	-	350
MoCo _x O _y -50	ZIF-67	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	50	12	350
MoCo _x O _y -100	ZIF-67	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	100	12	350
MoCo _x O _y -100-450°C	ZIF-67	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	100	12	450
MoCo _x O _y -100-550°C	ZIF-67	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	100	12	550
MoCo _x O _y -100-1h	ZIF-67	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	100	1	350
MoCo _x O _y -100-3h	ZIF-67	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	100	3	350
MoCo _x O _y -200	ZIF-67	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	200	12	350
Na ₂ MoO ₄ -MoCo _x O _y	ZIF-67	Na ₂ MoO ₄ ·2H ₂ O	140	12	350

2.3.5 Material Characterizations

Powder X-ray diffraction (XRD) patterns were obtained on a Bruker AXS D8 Advance X-ray diffractometer with Ni-filtered (2 μm thickness) Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 mA and 40 kV. Scanning electron microscopy (SEM) analysis was conducted with a Zeiss Auriga microscope (Carl Zeiss, Jena, Germany) equipped with an energy-dispersive X-ray spectroscopy (EDS) detector operating at 20 kV. Transmission electron microscopy (TEM) analysis was carried out using a field emission gun FEI™ Tecnai F20 microscope at 200 kV with a point-to-point resolution of 0.19 nm. Atomic force microscopy (AFM) measurements were conducted using an AFM Multimode 8 system attached to a Nanoscope V electronic unit (Bruker). Raman spectroscopy was carried out on a confocal Raman spectrometer (Renishaw in Via Qontor) equipped with a Leica DM2700M microscope over the range of 50 to 1200 cm^{-1} . A power of the laser of 1 mW cm^{-2} was kept at all samples. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Specs system (Specs GmbH, Berlin, Germany) equipped with an Al anode XR50 source operating at 150 W and a Phoibos 150 MCD-9 detector. The pressure in the analysis chamber was kept below 10^{-7} Pa. Thermogravimetric analyses (TGA) were carried out in air atmosphere from 50 to 700 $^{\circ}\text{C}$ with a ramp of 5 $^{\circ}\text{C min}^{-1}$ using a Diamond TG/DTA Instruments (PerkinElmer, Waltham, MA). EPR spectroscopy was conducted on a Bruker EMXplus instrument (Bruker, Germany) with a microwave frequency of 9.40 GHz at 100 K.

2.3.6 Electrode preparation and electrochemical measurements

Electrochemical To prepared the working electrodes, 2 mg of as-prepared catalyst was dispersed in a solution of 750 μL isopropanol and 220 μL deionized water. Then 30 μL Nafion (5 wt %) was added and the resulting solution was sonicated for at least 30 min until forming a homogeneous ink. After that, 5 μL of fresh catalyst ink was dropped onto a glassy carbon (GC, 3 mm in diameter) and naturally dried in air. The loading capacity was 0.145 mg cm^{-2} . All electrochemical measurements were performed at room temperature on a CHI760E electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China) using a standard three-electrode cell. A graphite rod was used as the counter electrode and Hg/HgO (1.0 M KOH) as the reference electrode. Linear sweep voltammetry (LSV) was conducted at a scan rate of 5 mV s^{-1} from 0 to 1.0 V (vs. Hg/HgO) in O_2 -saturated 1.0 M KOH electrolyte. All the presented data were corrected with 90%

iR-compensation. Electrochemical impedance spectroscopy (EIS) analysis was carried out in a frequency range from 100 kHz to 0.01 Hz at 5 mV and recorded at 1.55 V. The electrochemical double-layer capacitance (C_{dl}) curves were obtained by cyclic voltammetry (CV) in a non-Faradaic region (0.90–1.00 V vs. RHE) at scan rates in the range 20 to 200 mV s⁻¹ and using the following equation: $C_{dl} = \Delta j/v$, where Δj ($\Delta j = (j_a - j_c)/2$) and v are the current density (at 0.95 V, mA cm⁻²) and scan rate (mV s⁻¹), respectively. The electrochemical active surface area (ECSA) was determined by the equation: $ECSA = C_{dl}/C_s$, where C_s is the capacitance of an atomically smooth planar surface (in the range of 0.02 -0.06 mF cm⁻² in alkaline media, in this work, we used the $C_s=0.04$ mF cm⁻²). The long-term durability was tested using chronoamperometry at a constant current density of 10 mA cm⁻² for 60 h without iR compensation, and by comparing the LSVs curves (1.2 to 1.7 V) before and after 2000 CV cycles at a scan rate of 0.2 V s⁻¹. In-situ Raman spectra were collected after different CV cycles in the range 1.3 V to 1.7 V at a scan rate of 0.1 V s⁻¹) on an Xplora Plus Raman microscope (Horiba, France) with a 532 nm excitation wavelength. All obtained potentials (vs. Hg/HgO) were converted to the reversible hydrogen electrode (RHE) according to the Nernst equation: $E_{RHE} = E_{Hg/HgO} + 0.059 \text{ pH} + E^{\ominus}_{Hg/HgO}$, ($E^{\ominus}_{Hg/HgO} = 0.098\text{V}$). All corresponding current densities were normalized using the uniform geometrical area of the GC electrode (0.07 cm²). For all testing, a flow of O₂ was used to purge the electrolyte and guarantee the O₂/H₂O equilibrium at 1.23 V. The over-potentials (η) at 10 mA cm⁻² were calculated as follows: $\eta = E \text{ (vs. RHE)} - 1.23$, considering the O₂/H₂O equilibrium at 1.23 V.

2.4 Results and Discussion

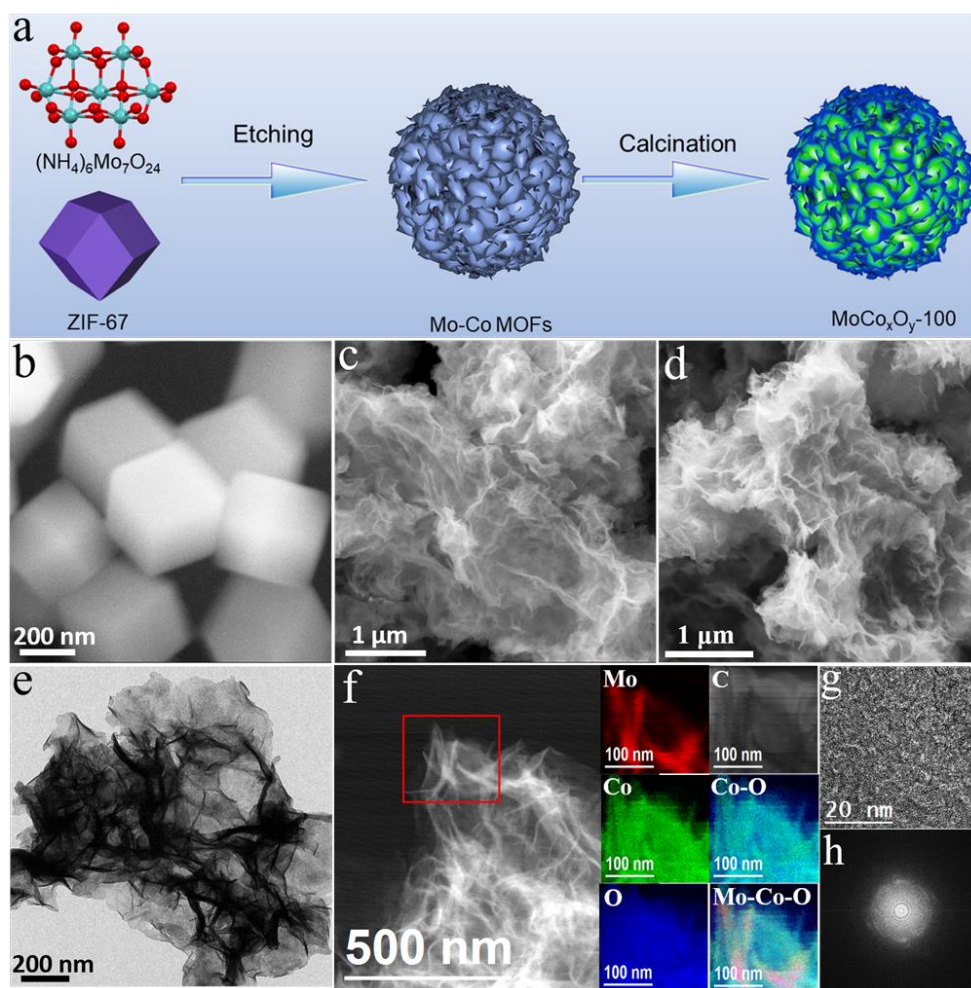


Figure 2.1. (a) Scheme of the synthetic route used to produce ultrathin amorphous MoCo_xO_y nanosheets. (b) SEM image of ZIF-67. (c) SEM image of Mo-Co MOF-100. (d) SEM, (e) TEM, (f) HAADF image and EELS chemical composition maps of MoCo_xO_y-100 nanosheets, obtained by using the Mo M_{4,5}-edges at 227 eV (red), Co L_{2,3}-edges at 779 eV (green), O K-edge at 532 eV (blue) and C K-edge at 284 eV (grey) and composites of Co-O and Mo-Co-O. (g) HRTEM image and (h) corresponding FFT spectrum of MoCo_xO_y-100 nanosheets.

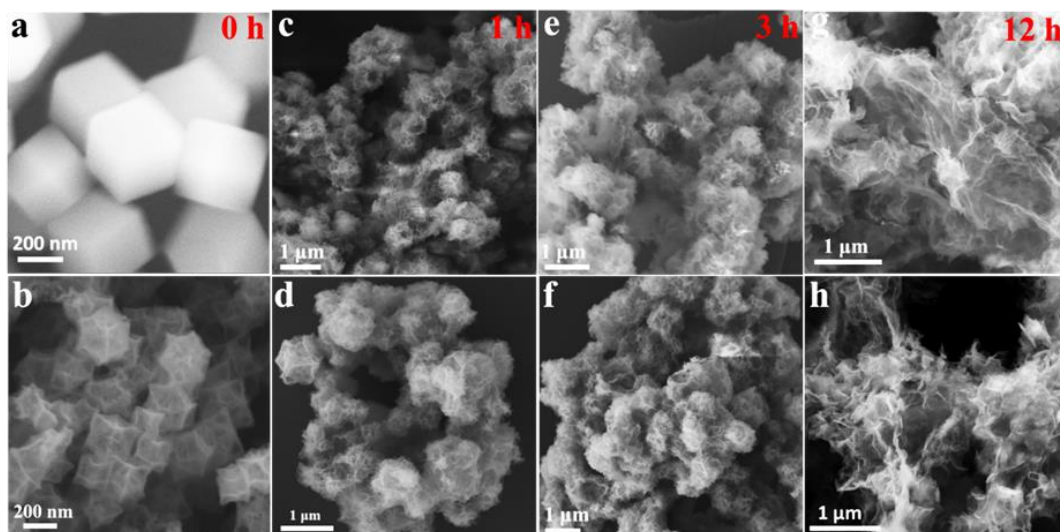


Figure 2.2. SEM images of a) ZIF-67, b) Co_3O_4 , c) Mo-Co MOFs-1h, d) MoCo_xO_y -100-1h, e) Mo-Co MOFs-3h, f) MoCo_xO_y -100-3h, g) Mo-Co MOFs-12h, and h) MoCo_xO_y -100-12h.

MOFs are crystalline materials with an ordered topological structure that are often used as template for the engineering of porous nanostructured electrocatalysts.⁵¹⁻⁵³ We combined this approach with the hydrolysis of an ammonium salt and the simultaneous MOF etching to prepare Mo-Co-based porous materials. A scheme of the synthesis process is displayed in Figure 2.1a. As precursor material, we selected a cobalt-based zeolitic imidazolate framework (ZIF-67). First, the template polyhedral ZIF-67 was prepared at room temperature following a reported procedure.^{49, 50} Subsequently, Mo-Co MOFs was obtained by ammonium molybdate hydrolysis and simultaneous etching of the ZIF-67. During this process, the hydrolysis of ammonium molybdate generates both protons (H^+) and hydroxides (OH^-). H^+ slowly etch the ZIF-67, releasing Co^{2+} ions. At the same time, OH^- promotes the precipitation of molybdate, cobalt ions and 2-methylimidazole to form an amorphous and layered material that we refer to as Mo-Co MOF. Finally, the obtained product was annealed at 350 °C for 2 h in air to obtain a Mo-doped cobalt oxide, MoCo_xO_y .

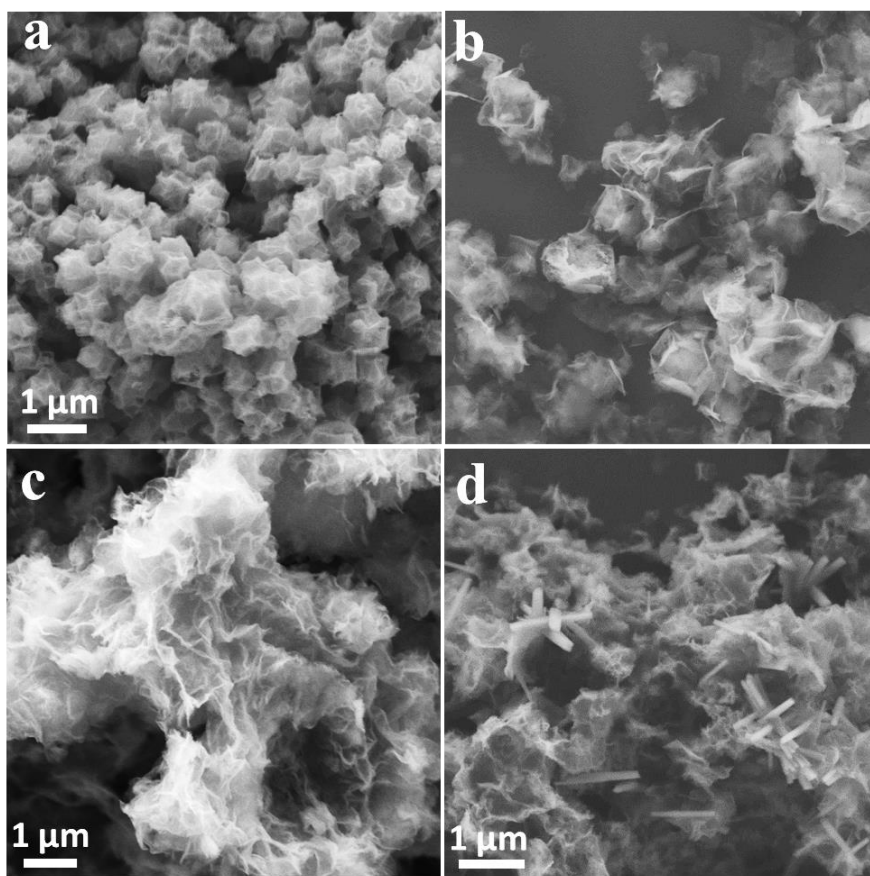


Figure 2.3. SEM images of a) Co_3O_4 , b) $\text{MoCo}_x\text{O}_y\text{-50}$, c) $\text{MoCo}_x\text{O}_y\text{-100}$ and d) $\text{MoCo}_x\text{O}_y\text{-200}$.

Figure 2.1b displays a representative scanning electron microscopy (SEM) image of the ZIF-67 template, which shows a smooth rhombic dodecahedron morphology with a uniform particle size of about 350 nm, and high crystallinity, as observed by powder X-ray diffraction (XRD) analysis. As the hydrolysis takes place, Mo-Co MOF nanosheets begin to appear and progressively expand around the ZIF-67 template, which gradually disappears (Figure 2.2). Eventually, after 12 h reaction, the dodecahedron template has fully disappeared and only wrinkled nanosheets are observed (Figure 2.1c and Figure 2.2g).

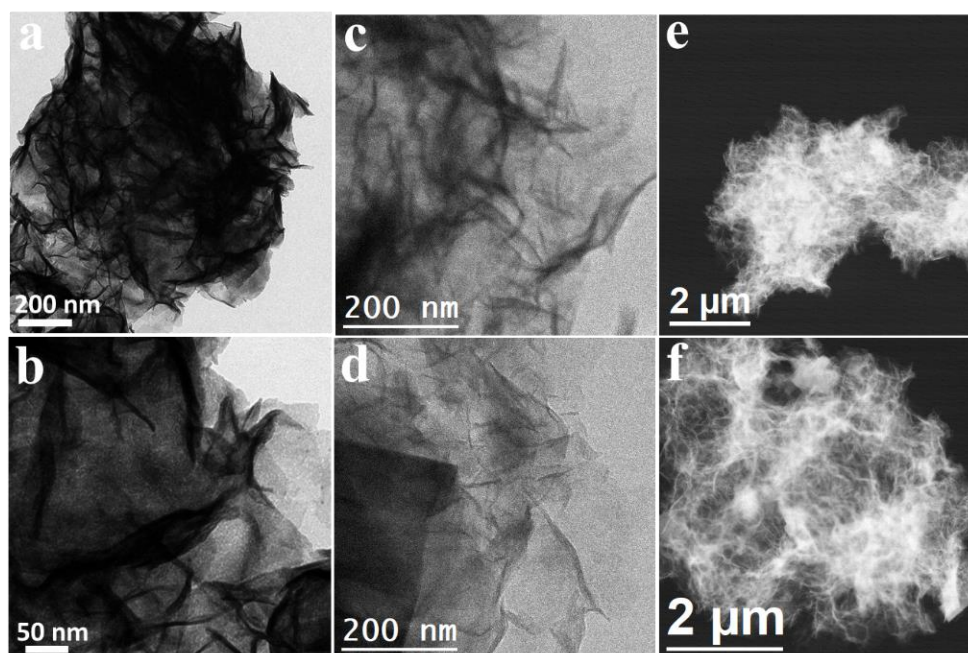


Figure 2.4 (a-d) TEM and (e-f) HAADF STEM images of $\text{MoCo}_x\text{O}_y\text{-100}$.

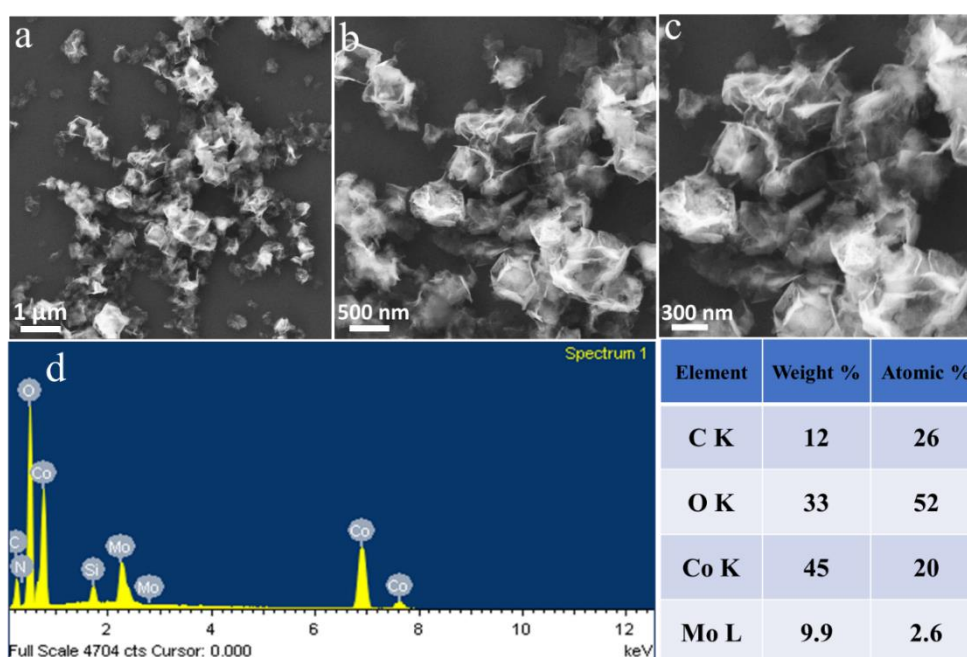


Figure 2.5. a-c) SEM images and b) EDX spectrum of $\text{MoCo}_x\text{O}_y\text{-50}$ after 350 °C calcination

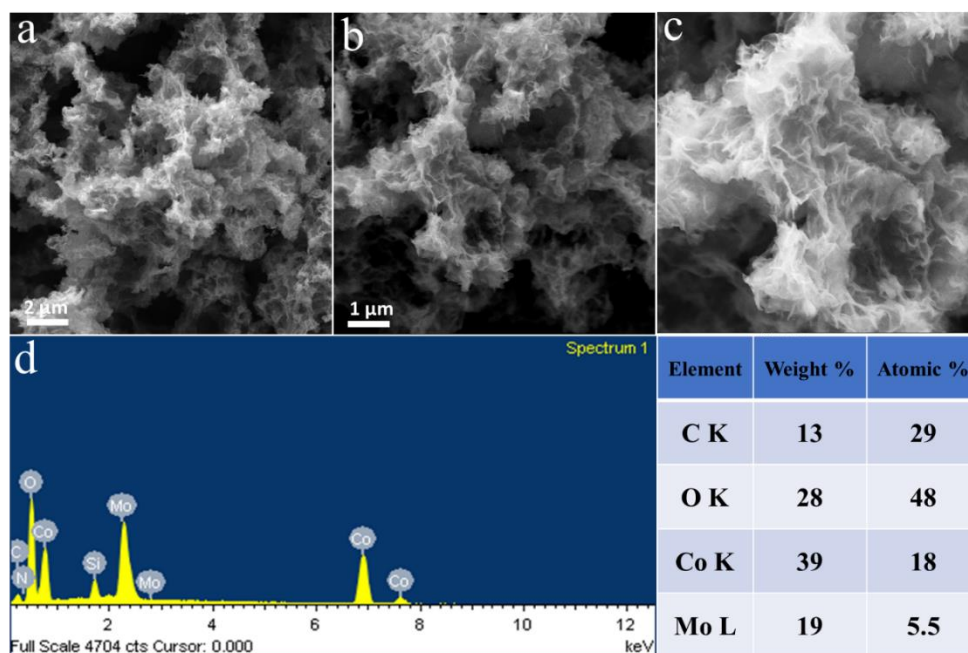


Figure 2.6. a-c) SEM images and d) EDX spectrum of MoCo_xO_y -100 after 350 °C calcination

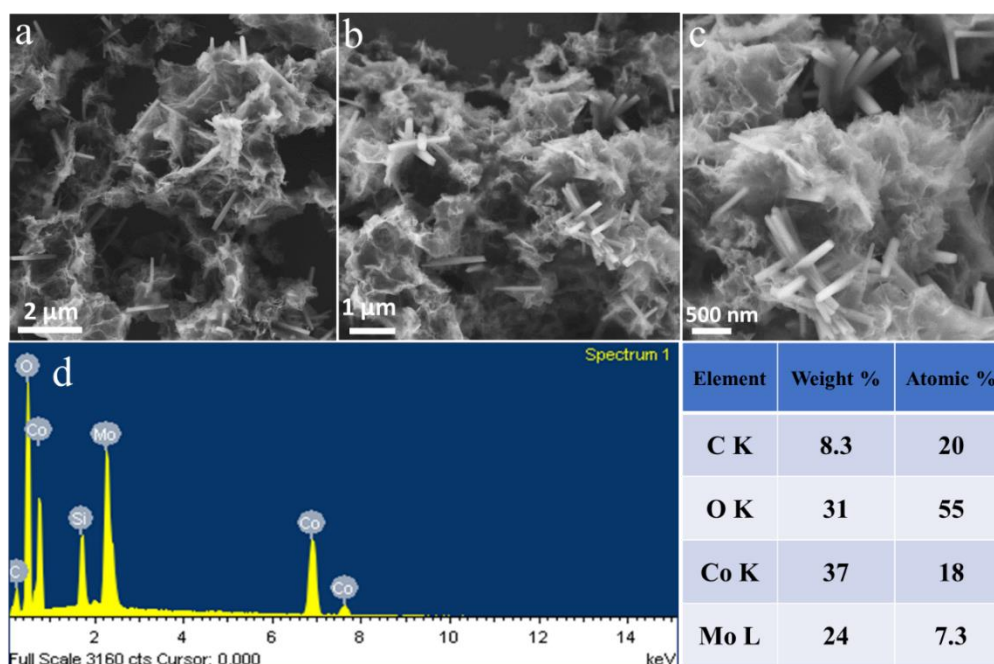


Figure 2.7. a-c) SEM images and d) EDX spectrum of MoCo_xO_y -200 after 350 °C calcination.

The amount of ammonium molybdate plays a critical role in the morphology of the obtained material. Small amounts of ammonium molybdate (50 mg) do not generate enough protons to entirely consume the ZIF-67 templates, thus resulting in ZIF-67 dodecahedrons with gentle surface wrinkles (Figure 2.3b). This incomplete etching was confirmed by XRD patterns, which displayed the peaks of ZIF-67 in Mo-Co MOFs

obtained with 50 mg ammonium molybdate. As the amount of ammonium molybdate increases, the formed Mo-Co MOFs-100 and Mo-Co MOFs-200 gradually become amorphous. On the other hand, when an excess amount of ammonium molybdate is used, some elongated rods, probably MoO_3 coming from the decomposition of the excess of ammonium molybdate, are formed (Figure 2.3d).

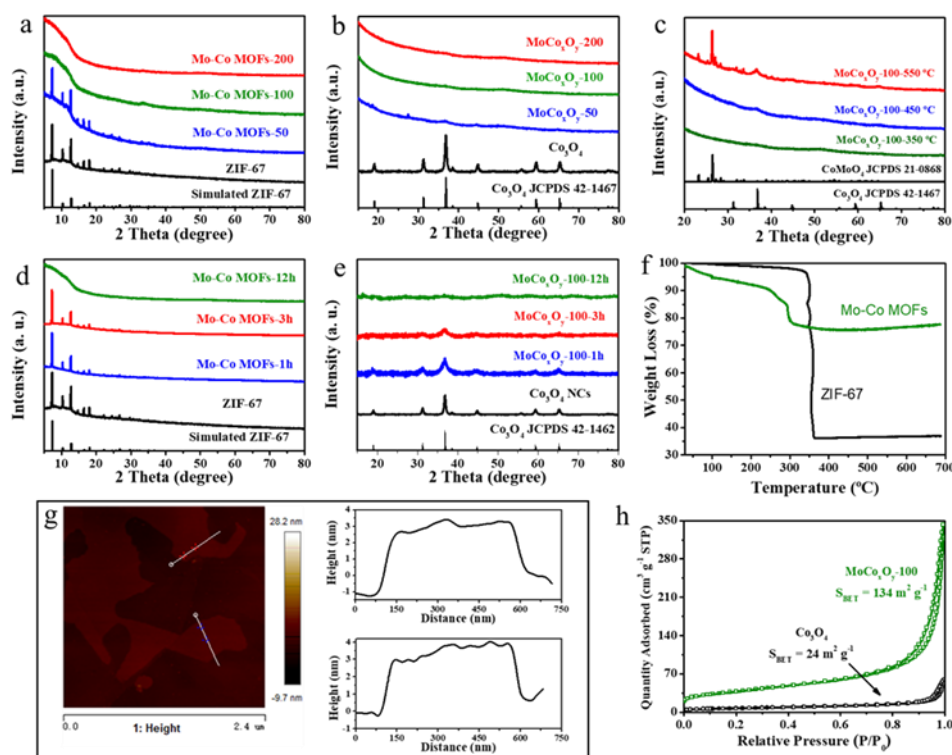


Figure 2.8. (a-e) XRD patterns of the initial MOFs (a), the annealed MoCo_xO_y samples (b), MoCo_xO_y -100 after different annealing temperature (c), Mo-Co MOFs produced using different stirring times (d), and MoCo_xO_y -100 samples obtained from the annealing of Mo-Co MOFs produced with different stirring times (e). f) TGA curve under air atmosphere of ZIF-67 and Mo-Co MOFs. g) AFM images and the corresponding thickness measurement data of MoCo_xO_y -100. h) N_2 adsorption-desorption isotherms for MoCo_xO_y -100.

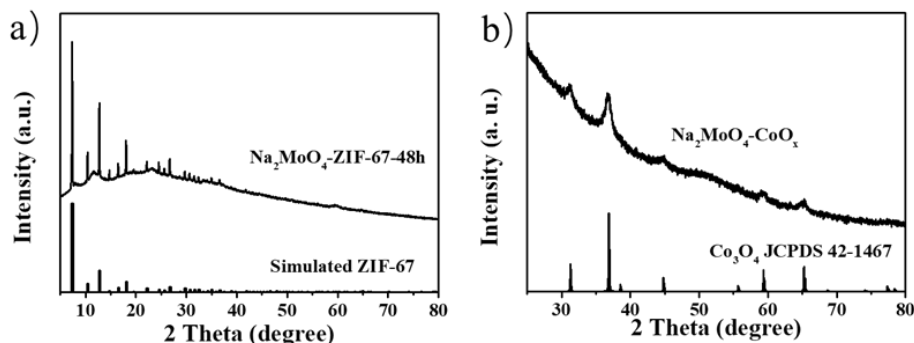


Figure 2.9. XRD patterns of a) Na_2MoO_4 -ZIF-67 and b) Na_2MoO_4 - CoO_x after 350 °C calcination.

Thermogravimetric analysis (TGA) shows weight loss steps at 300 °C and 350 °C for ZIF-67 and Mo-Co MOFs, respectively (Figure 2.8c). Thus, we selected 350 °C as the annealing temperature to remove unstable organic ligands but minimizing the loss of carbon, which will aid to promoting the electrical conductivity of the final material. Annealing the material at 350 °C in air did not allow its crystallization, thus the annealed Mo-Co MOFs maintained their amorphous atomic architecture, as observed by XRD (Figure 2.9b). After annealing, the nanosheet morphology was also maintained (Figure 2.1e, Figure 2.6). Atomic force microscopy (AFM) analysis showed the average thickness of the MoCo_xO_y nanosheets to be ca. 4 nm (Figure 2.8e). Besides, high-resolution TEM (HRTEM) images and the corresponding indexed fast Fourier transform (FFT) crystallographic analyses confirmed the annealed MoCo_xO_y -100 nanosheets to present no crystallographic ordering. This is in contrast with the good crystallinity of Co_3O_4 nanocrystals obtained by annealing the precursor ZIF-67 at the same temperature (Figure 2.8b). Meanwhile, an annular dark-field scanning transmission electron microscope images (HAADF-STEM) and electron energy loss spectroscopy (EELS) mapping showed Mo, Co and O elements to be homogeneously distributed throughout the nanosheets (Figure 2.1f).

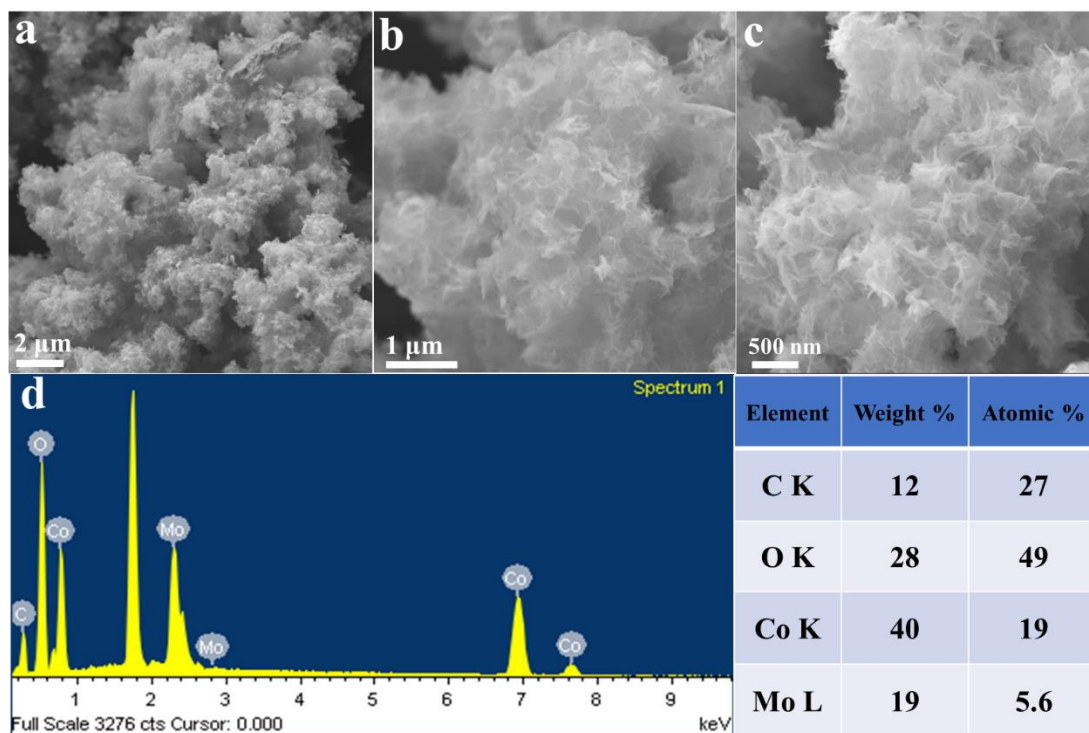


Figure 2.10. a-c) SEM images and d) EDX spectrum of MoCo_xO_y -100 after 450 °C calcination

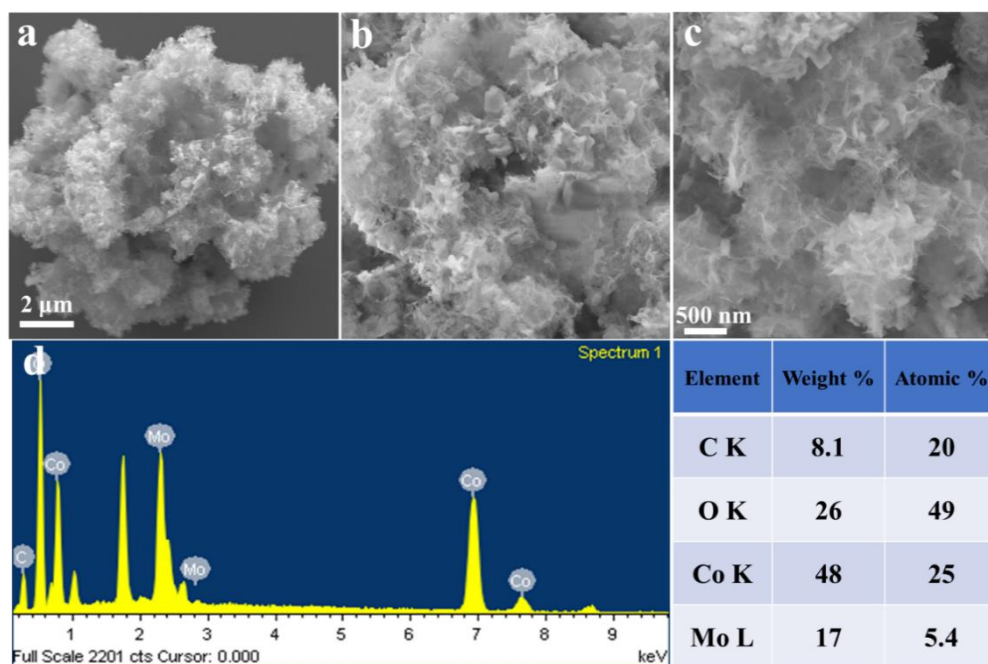


Figure 2.11. a-c) SEM images and d) EDX spectrum of $\text{MoCo}_x\text{O}_y\text{-100}$ after 550 °C calcination

Increasing the annealing temperature allowed to partially crystallize the material. Figure 2.8c displays the XRD pattern of $\text{MoCo}_x\text{O}_y\text{-100}$ annealed at higher temperatures, up to 550 °C. Amorphous oxide nanosheets transform into weakly crystalline Co_3O_4 at 450 °C and become a mixture of CoMoO_4 and Co_3O_4 with good crystallinity at 550 °C. Higher temperatures caused the partial collapse of the nanosheet geometry (Figure 2.10, 2.11).

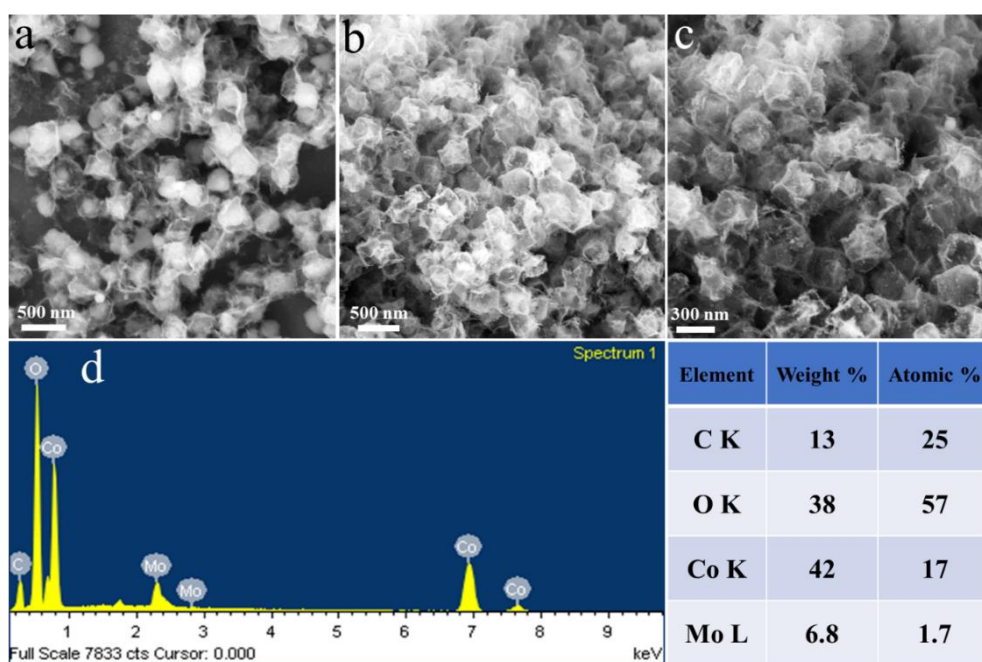


Figure 2.12. a) SEM images of $\text{Na}_2\text{MoO}_4\text{-ZIF-67}$. b-c) SEM images and d) EDX spectrum of $\text{Na}_2\text{MoO}_4\text{-CoO}_x$ after 350 °C calcination.

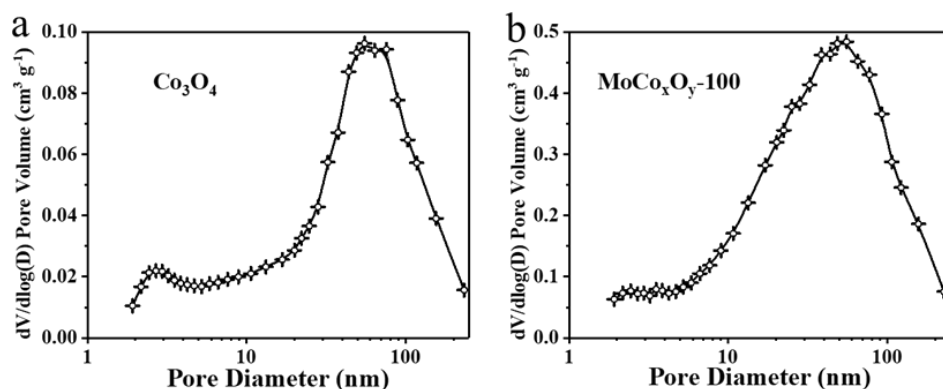


Figure 2.13. Pore size distribution for a) Co_3O_4 and b) $\text{MoCo}_x\text{O}_y\text{-100}$

The source of molybdenum also has a huge impact on the product morphology. Using sodium molybdate as the molybdenum source, polyhedral ZIF-67 structures were maintained even after 48 h reaction (Figure 2.9a). After annealing this material in air, crystalline Co_3O_4 nanocages were obtained (Figure 2.9b, 2.12b, c), but EDS analysis showed the amount of molybdenum in these nanocages to be relatively low (Figure 2.12d). MoCo_xO_y displays type-IV nitrogen adsorption-desorption isotherms with an H3-type hysteresis loop at high relative pressures (0.8–1.0 P/P_0 , Figure 2.8d). Isotherms provided a Brunauer–Emmett–Teller (BET) specific surface area of 134 $\text{m}^2 \text{g}^{-1}$ for $\text{MoCo}_x\text{O}_y\text{-100}$ and just 24 for the Co_3O_4 nanoparticles. Besides, the Barrett-Joyner-Halenda (BJH) average pore size and cumulative pore volume were 15.8 nm and 0.53 $\text{cm}^3 \text{g}^{-1}$ for $\text{MoCo}_x\text{O}_y\text{-100}$, and 17.2 nm and 0.09 $\text{cm}^3 \text{g}^{-1}$ for Co_3O_4 nanoparticles (Figure 2.13). These results indicate that $\text{MoCo}_x\text{O}_y\text{-100}$ is characterized by a suitable mesoporous structure to provide a high electroactive surface area and at the same time facilitate the transport rate of reactants and reaction products.^{50, 51}

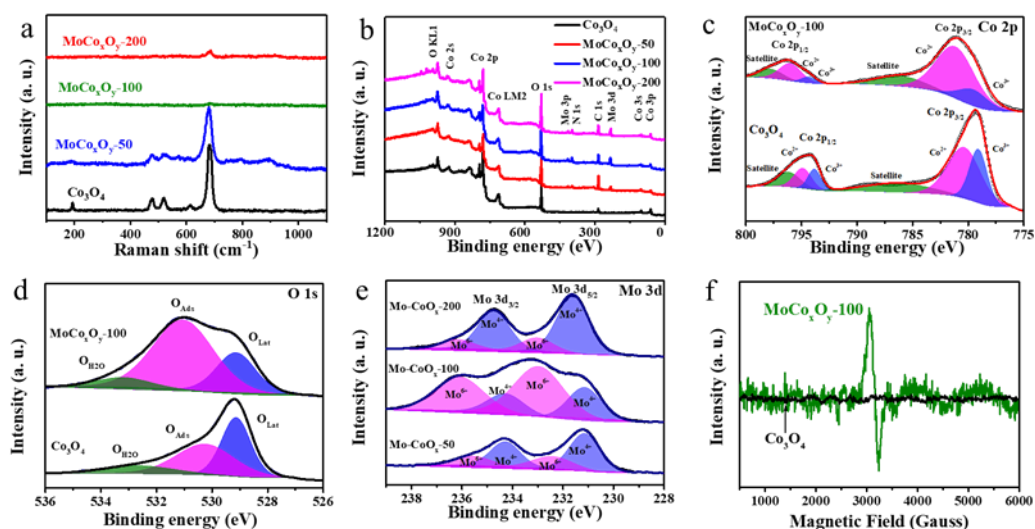


Figure 2.14. Raman and b) survey XPS spectra of Co_3O_4 and MoCo_xO_y samples. c) Co 2p, d) O 1s and e) Mo 3d high-resolution XPS spectra and f) EPR spectra of Co_3O_4 and MoCo_xO_y -100.

Figure 2.14a shows the Raman spectra of Co_3O_4 and MoCo_xO_y obtained from the annealing of ZIF-67 and Mo-Co MOF, respectively. Four obvious peaks were observed in the Co_3O_4 spectrum at 185.5, 465.3, 506.6, and 670 cm^{-1} , which were associated with the F^1_{2g} , E^2_{g} , F^2_{2g} , and A^1_{g} phonon modes of crystalline Co_3O_4 .^{52, 53} With the introduction of Mo, the peaks associated with the Co_3O_4 phase gradually disappeared, confirming the amorphous nature of the formed materials. X-ray photoelectron spectroscopy (XPS) analysis showed the presence of elemental C, N, O, Co and Mo in all MoCo_xO_y samples (Figure 2.14b), which is consistent with EDS analysis. The high-resolution Co 2p XPS spectra were fitted considering two Co chemical environments, at ca. 779.4 eV ($2p_{3/2}$) and 781.5 eV ($2p_{3/2}$), resembling those of Co within lattice Co_3O_4 and a hydroxide-like environment, respectively (Figure 2.14c and 2.15).⁵⁴ The lattice Co_3O_4 component was majoritarian in most of the samples, but the hydroxide-like component was dominant in MoCo_xO_y -100. Table S2 displays the ratio of the different surface Co chemical states as determined by XPS analysis.

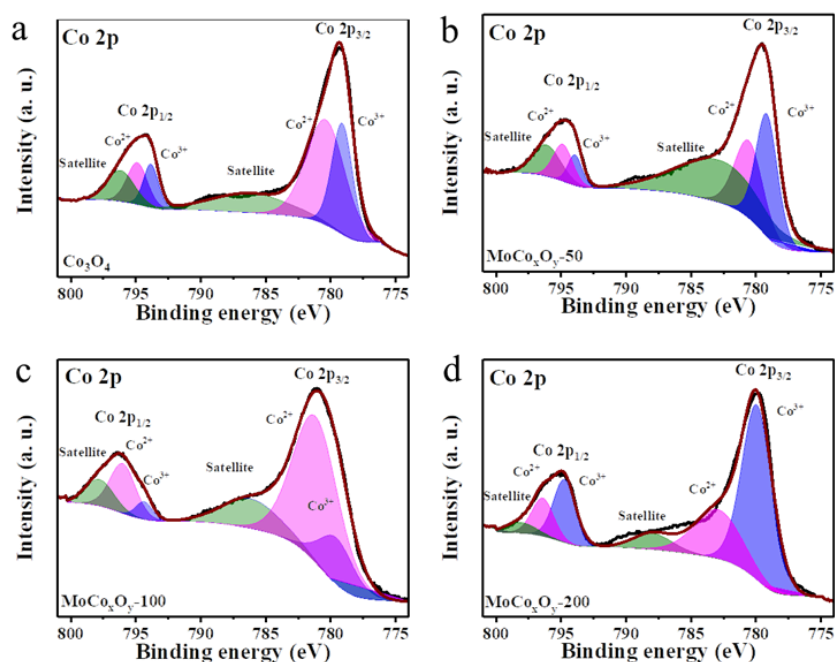


Figure 2.15. a-d) Co 2p high-resolution XPS spectra of Co_3O_4 and MoCo_xO_y with different molybdenum contents.

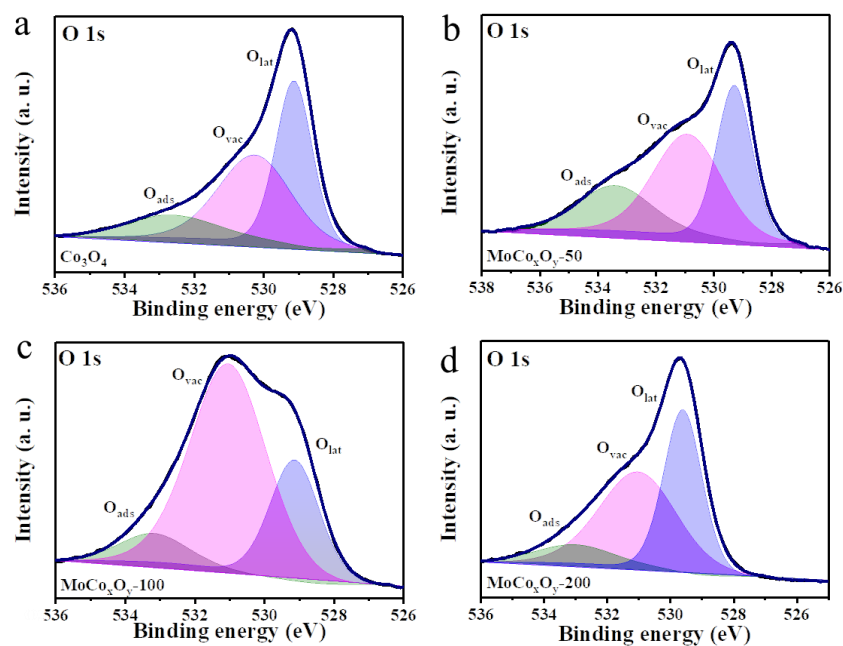


Figure 2.16. a-d) O 1s high-resolution XPS spectra of Co_3O_4 and MoCo_xO_y with different molybdenum contents.

Table S2. Surface ratios of Co and Mo chemical states, ratio of adsorbed vs. lattice oxygen, and Mo/Co ratio as obtained from the XPS analysis.

Samples	$\text{Co}^{2+}/\text{Co}^{3+}$	$\text{Mo}^{4+}/\text{Mo}^{6+}$	$\text{O}_{\text{ads}}/\text{O}_{\text{lat}}$	Mo/Co
Co_3O_4	3.06	-	0.62	0

MoCo_xO_y-50	1.96	3.3	0.66	0.21
MoCo_xO_y-100	0.45	0.76	1.48	0.48
MoCo_xO_y-200	1.33	4.2	0.56	0.29

The asymmetric high-resolution O 1s XPS spectra were fitted with three nearly Gaussian bands (Figure 2.14d and 2.16). The O_{lat} component, at 529 eV, is attributed to O²⁻ within a metal oxide lattice. The O_{ads} component at 531 eV, is associated with hydroxide ions (OH⁻) and/or other chemisorbed and dissociated oxygen species (O²⁻, O₂²⁻, or O⁻), and its intensity is frequently related to the concentration of oxygen vacancies. Finally, the O_{H2O} component at around 533 eV is usually attributed to adsorbed water.^{20, 42, 55} As displayed in table S2, the relative amount of chemisorbed species is significantly higher in MoCo_xO_y-100 (O_{ads}/O_{lat}=1.48) than in Co₃O₄ (O_{ads}/O_{lat}=0.62), consistent with the Co 2p XPS spectra. These results indicate the formation of a more extended oxyhydroxide surface layer and/or a higher concentration of adsorbates on samples containing molybdenum, which could be related to a larger concentration of oxygen vacancies.^{56, 57} Figure 2.14e displays the high-resolution XPS spectra of Mo 3d. The spectra were fitted with two doublets, associated with Mo⁴⁺ (Mo 3d_{5/2} at 231 eV) and Mo⁶⁺ (Mo 3d_{5/2} at 233 eV) chemical environments.^{6, 24} As displayed in Table S2, the Mo⁴⁺ component was dominant at the surface of all samples, except for MoCo_xO_y-100 that displayed a higher concentration of Mo⁶⁺: Mo⁴⁺/Mo⁶⁺=0.76. The EPR spectra of MoCo_xO_y-100 displays the footprint of oxygen vacancies at g=2.12 (Figure 2.14f). This signal was not observed for Co₃O₄, which points to the key role played by Mo cations in the generation of oxygen vacancies. Notice that the presence of oxygen vacancies has associated the existence of high-energy dangling bonds, which could promote surface chemisorption, as observed from XPS results, and electrocatalytic performances.^{15, 28, 29, 58-60}

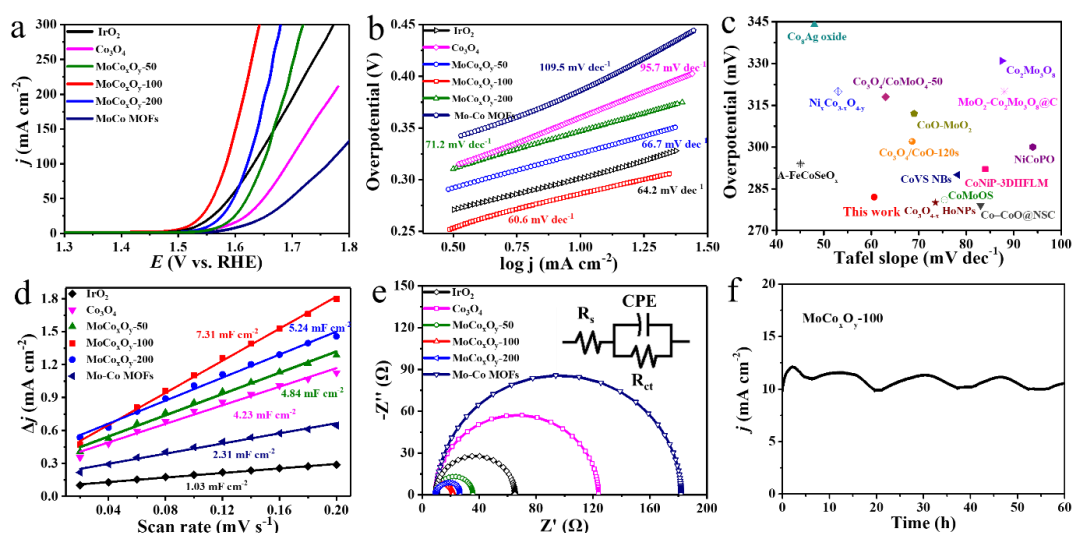


Figure 2.17. (a-d) Electrocatalytic OER performance of the various catalysts. a) LSV curves. b) Tafel plots. c) Comparison of overpotential at 10 mA cm^{-2} and Tafel slopes for MoCo_xO_y -100 and some cobalt-based OER catalysts (Table S6). d) Capacitive current density measured at 0.95 V vs. RHE plotted as a function of scan rate. e) Nyquist plots at the potential of 1.55 V vs. RHE. f) Chronoamperometry curve of MoCo_xO_y -100.

Table S3. Comparison of OER activity of obtained catalyst.

Catalyst	η_{10} [mV]	Tafel Slope [mV dec^{-1}]
IrO_2	301	66.7
Co_3O_4	350	95.7
MoCo_xO_y -50	344	71.2
MoCo_xO_y -100	282	60.6
MoCo_xO_y -200	322	64.2
Co-Mo MOFs	379	109.5

The OER electrocatalytic performance of the materials was initially evaluated by linear sweep voltammetry (LSV) in 1.0 M KOH (Figure 2.17a). A commercial IrO_2 catalyst was also measured as a reference. Among the tested samples, MoCo_xO_y -100 exhibited the lowest onset potential and the highest current densities. MoCo_xO_y -100 was characterized by an overpotential of 282 mV at a current density of 10 mA cm^{-2} (η_{10}), well below that of IrO_2 (301 mV), Co_3O_4 (350 mV) and Mo-Co MOFs (379 mV). As depicted in Figure

2.17b, the Tafel slope of $\text{MoCo}_x\text{O}_y\text{-100}$ (60.6 mV dec^{-1}) was also well below that of IrO_2 (66.9 mV dec^{-1}), proving the more favourable and faster reaction kinetic of the former.

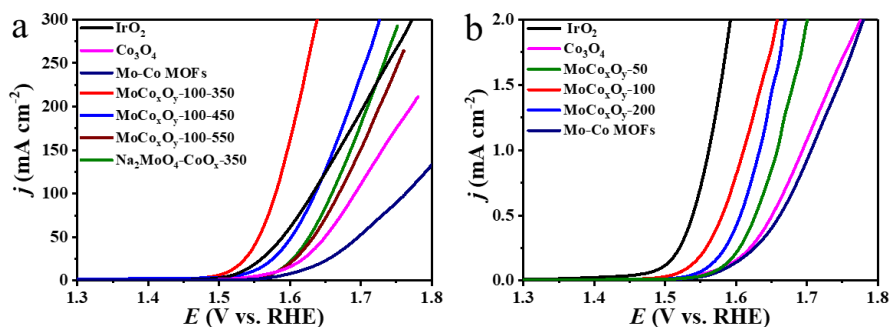


Figure 2.18. a) OER polarization curves for $\text{MoCoO}_x\text{-100}$ annealed at different temperatures and $\text{Na}_2\text{MoO}_4\text{-CoO}_x$. b) ECSA-normalized OER polarization curves for Mo-Co MOFs, IrO_2 , Co_3O_4 , $\text{MoCoO}_x\text{-50}$, $\text{MoCoO}_x\text{-100}$ and $\text{MoCoO}_x\text{-200}$ in 1.0 M KOH.

Comparing materials annealed at different temperatures (Figure 2.18a), we observed the catalyst obtained at 350°C to provide the best OER performance. Besides, the molybdenum content also played an important role, with $\text{MoCoO}_x\text{-100}$ displaying superior performance than $\text{MoCoO}_x\text{-50}$ and $\text{MoCoO}_x\text{-200}$ samples (Figure 2.17 and 2.18b). Additionally, we observed the molybdenum source to have a strong influence on the performance of the catalyst, with the material obtained using ammonium molybdate etching displaying a significantly superior performance than the material obtained with sodium molybdate (Figure 2.18a).

The outstanding performance of $\text{MoCoO}_x\text{-100}$ is demonstrated when comparing the η^{10} and Tafel slope of $\text{MoCoO}_x\text{-100}$ with those of other cobalt-based electrocatalysts (Table S5 and Figure 2.17c). This outstanding OER performance is attributed to the high density of active sites derived from the amorphous and defective layered nanosheet structure, and potentially to the Mo-activated participation of lattice oxygen in the OER, as discussed below. The charge transfer rate at the catalyst reaction interface was evaluated by electrochemical impedance spectroscopy (EIS).^{6, 60} Nyquist plots show the charge transfer resistance (R_{ct}) of $\text{MoCoO}_x\text{-100}$ to be the smallest among all the tested samples (Figure 2.17e), which point at a faster charge transfer rate in this material.

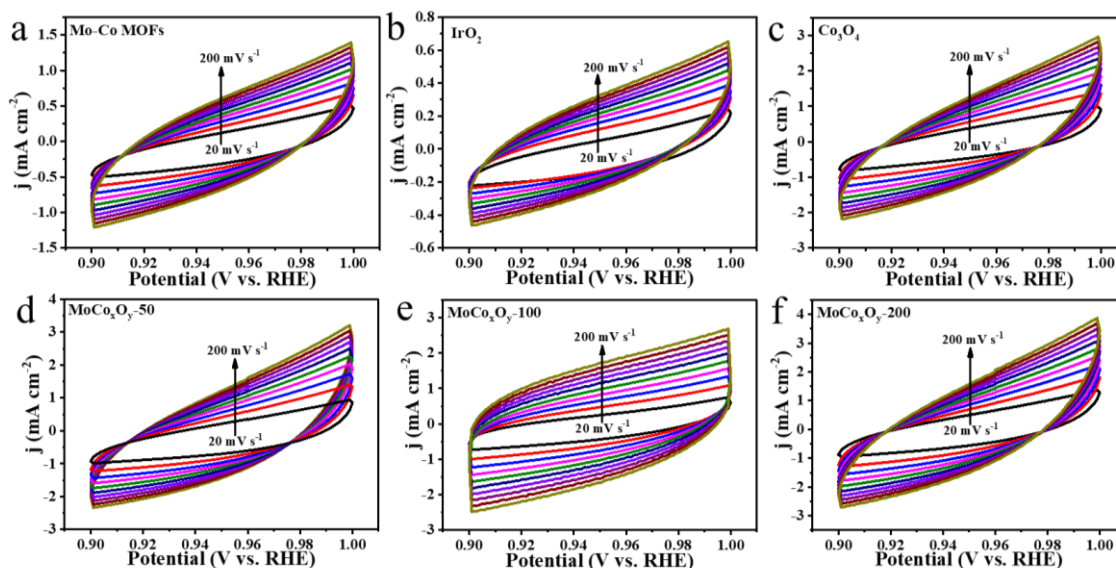


Figure 2.19. Cyclic voltammograms for a) Mo-Co MOFs; b) IrO₂; c) Co₃O₄ and d) MoCo_xO_y-50; e) MoCo_xO_y-100; f) MoCo_xO_y-200 in the non-faradaic region of 0.90-1.00 V vs. RHE at various scan rates.

Table S4. C_{dl} and ECSAs of various catalysts.

Catalyst	C_{dl} (mF cm ⁻²)	ECSA (cm ⁻²) ^a
IrO ₂	1.03	25.75
Co ₃ O ₄	4.23	105.75
MoCo _x O _y -50	4.84	121.00
MoCo _x O _y -100	7.31	182.75
MoCo _x O _y -200	5.24	131.00
Co-Mo MOFs	2.31	57.75

ECSA is the area accessible to the electrolyte ion and it is generally proportional to the electrocatalysts double-layer capacitances (C_{dl}), which was determined from CVs at different scan rates, from 20 mV s⁻¹ to 200 mV s⁻¹ (Figure 2.19). As shown in Figure 2.17d, MoCo_xO_y-100 displays the largest C_{dl} value (7.36 mF cm⁻²), well above that of MoCo_xO_y-50, MoCo_xO_y-200, Co₃O₄ and Mo-Co MOFs. The enhanced C_{dl} indicates that MoCo_xO_y-100 exposes a larger number of active sites. When normalizing to ECSA, significantly higher current densities were still obtained for MoCo_xO_y-100 compared with the other materials, which further demonstrated the higher OER activity of this material, beyond its higher active surface area (Figure 2.18b).

Beyond some minor fluctuations associated with the formation of bubbles and temperature oscillations in the laboratory, the chronoamperometric (i-t) durability test showed an almost negligible current change for MoCo_xO_y-100 electrodes after 60 h of operation (Figure 2.17f). Meantime, very similar polarization curves were obtained for MoCo_xO_y-100 before and after 2000 cycles, with almost zero attenuation of the cathodic current (Figure 2.20a). These results demonstrate the excellent stability toward the OER process of MoCo_xO_y-100.

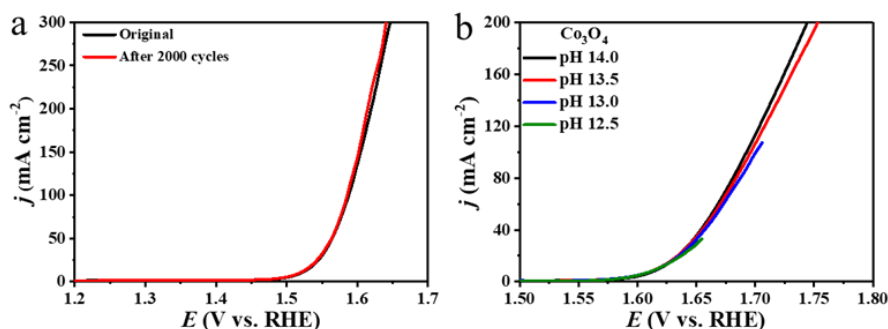


Figure 2.20. OER polarization curves of a) MoCo_xO_y-100 before and after 2000 cycles. b) Co₃O₄ at different pH values.

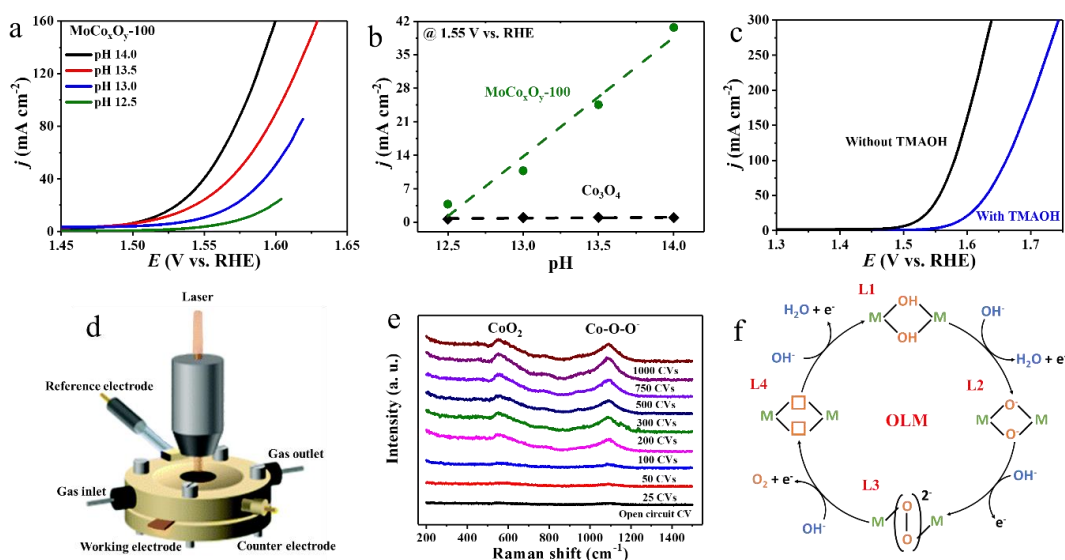


Figure 2.21. (a) OER polarization curves of MoCo_xO_y-100 for pH dependence activities. (b) Current densities MoCo_xO_y-100 and Co₃O₄ at 1.5 V vs. RHE as a function of the pH value. (c) OER Polarization of MoCoxOy-100 in 1 M KOH without and with TMAOH, respectively. (d) Schemes of in-situ Raman spectrometry. (e) In situ Raman spectra of MoCo_xO_y-100 after different CV cycles in 1.0 M KOH electrolyte. (f) Proposed OER mechanism of lattice oxygen participation (LOM), where □ represents an oxygen vacancy.

Within a basic aqueous solution, the surface of Co-based electrocatalysts tends to be oxidized into cobalt oxyhydroxide (CoOOH), which is considered the active OER phase.²⁵ Some previous studies concluded that CoOOH catalysed the OER through a LOM.⁶¹ In an oxyhydroxide (M-OOH), the LOM involves several steps as simplified in Figure 5.21f.^{60, 62} Briefly, the first steps involve the interaction with hydroxide ions in solution, the deprotonation of OH⁻ groups within the oxyhydroxide, and the release of H₂O. Subsequently, O–O bonds are formed within the oxide structure and O₂ is released. The release of O₂ leaves oxygen vacancies behind, which are filled through the adsorption of additional OH⁻, returning the catalyst to its initial state.

A fundamental characteristic of LOM is the direct O-O coupling, which bypasses the need for a correlated intermediate adsorption in the AEM. Thus, to distinguish LOM from AEM one can track the generation of peroxo-like (O₂²⁻) and superoxo-like (O²⁻) species. To track the existence of these negatively charged oxygenated species, tetramethylammonium cation (TMA⁺) was introduced as a chemical probe into the KOH solution (1M KOH +1M TMAOH). TMA⁺ specifically binds with negative oxygenated species, thus hamper the OER via LOM. As shown in Figure 5.21c, when introducing TMAOH into the KOH solution, the OER activity of MoCo_xO_y-100 was seriously reduced, which demonstrates the key contribution played by LOM in this material.

Besides, LSV measurements with electrolytes with different KOH concentrations, from 0.032 M (pH 12.5) to 1 M (pH 14.0), were used to investigate the dependence of OER activity on pH (Figure 5.21a, b). We observed the MoCo_xO_y-100 electrocatalyst at 1.55 V vs RHE to exhibit a strong pH-dependent OER activity on the RHE scale (25 mA cm⁻² pH⁻¹). In contrast, Co₃O₄ showed a mostly pH-independent OER activity as this same potential (0.18 mA⁻² pH⁻¹, Figure 5.20b). A strong pH-dependent OER activity on the RHE scale is a distinct feature of LOM, associated with its decoupled proton and electron transfer steps.^{28, 61, 64, 65} The observed activity increase can be intuitively understood by the easier deprotonation of the OH groups of the oxyhydroxide structure when increasing pH.¹⁷

Operando Raman spectroscopy was used to gain additional inside of the reaction kinetics in our MoCo_xO_y-100 catalyst and determine the active species during OER. After 200 CV cycles and above, we observed the appearance of a broad peak at 550-600 cm⁻¹, corresponding to A_{1g} and E_g vibrational modes of Co-O in CoOOH.^{66 67} Besides, an

additional broad band was observed in the 1000-1200 cm^{-1} range (peaking at ca. 1090 cm^{-1}), which is assigned to a superoxidic specie (CoOO^-).⁶¹ The intensity of these bands increased with the CV cycle times, demonstrating the generation and progressive accumulation of these species during the OER process.

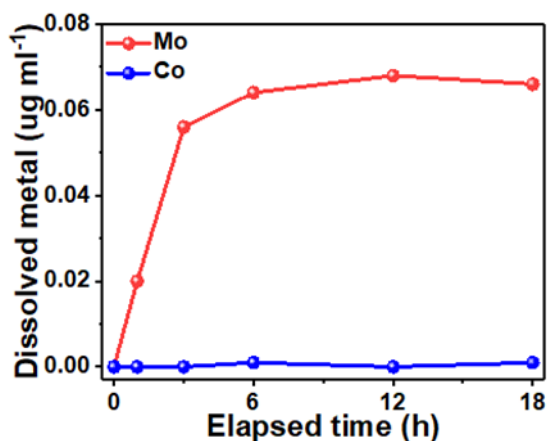


Figure 2.22. Time-dependent concentration of dissolved Mo and Co in the electrolyte of MoCo_xO_y -100.

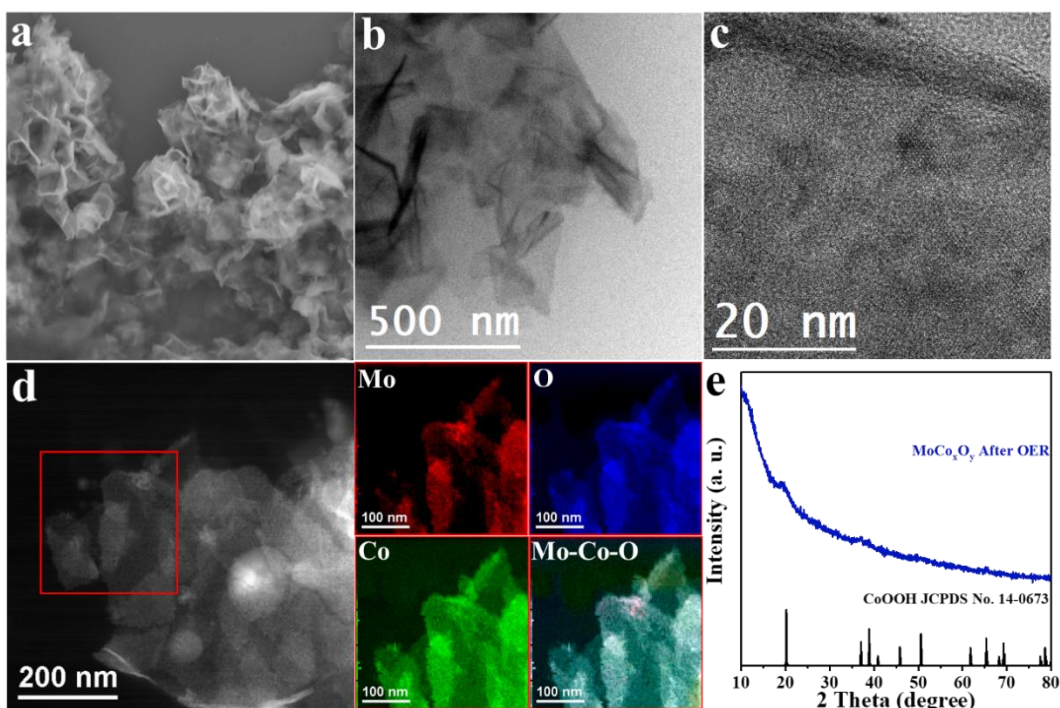


Figure 2.23. (a) SEM, (b) TEM, (c) HRTEM, (d) HAADF image and EELS chemical composition maps, (e) XRD pattern of MoCo_xO_y nanosheets after long-time durability test.

To confirm the transformation, we also analyse the content of Mo and Co in the electrolyte by inductively coupled plasma- mass spectrometry (ICP-MS). As shown in

Figure 5.22, the result shows that the content of Co keeps at a low level throughout the process. In contrast, the content of Mo increases with time and reaches the summit after 6 h electrolysis. Dissolution or leaching out of Mo occurs, which results in metal vacancies and cobalt hydroxide formation.⁶⁸ However, structural destruction of nanosheet does not occur, and the morphology of the nanosheet is preserved after the long-term OER process (Figure 5.23). Figures 5.23c and 5.23e show an HRTEM micrograph of the post-OER product with obvious lattice fringes and the XRD pattern of the material displaying a distinct diffraction peak, which was identified as γ -CoOOH. SEM and TEM images exhibited the ultrathin nanosheet structure to be maintained, without any obvious change after OER cycling (Figure 5.23a, b). Moreover, both EDS elemental mappings and the HAADF-STEM images (Figure 5.23d) demonstrate the homogenous distribution of Co, O and Mo in the cycled material, in which Mo-atoms were doped onto the outermost surfaces of γ -CoOOH.

Table S5. Comparison of OER activity of amorphous MoCo_xO_y -100 nanosheets with recently reported Co-based electrocatalysts in alkaline electrolyte.

Catalyst	Electrolyte	Loading	η_{10}	Tafel Slope	References
		[mg cm^{-2}]	[mV]	[mV dec^{-1}]	
MoCo_xO_y-100	1.0 M KOH	0.15	282	60.4	This work
A-FeCoSeO_x-100	1.0 M KOH	0.27	294	45.1	66
Co₃O₄/CoMoO₄-50	1.0 M KOH	0.26	318	63	67
Co-LDH FNSAs	1.0 M KOH	/	300	110	68
MoO₂-Co₂Mo₃O₈	1.0 M KOH	0.20	320	88	69
CoVS NBs	1.0 M KOH	0.30	290	78.2	70
Co₂Mo₃O₈	1.0 M KOH	0.14	290	87.5	71
Co₈Ag oxide	1.0 M KOH	0.12	344	48	72
NiCoPO/NC	1.0 M KOH	0.21	300	94	73
Co₃O_{4-x} HOPNPs	0.1 M KOH	/	280	73.5	74
CoO-MoO₂	1.0 M KOH	0.5	312	75	75
Co₃O₄/CoO-120s	1.0 M KOH	/	302	68.6	76
CoNiP-3DHFLMs	1.0 M KOH	0.13	292	98	77
3D CoMoOS NBs	1.0 M KOH	/	281	75.4	78

Co-CoO@NSC-5	1.0 M KOH	0.25	279	83	79
Ni _x Co _{3-x} O _{4-y}	1.0 M KOH	0.36	320	53	80

2.5 Conclusions

We detailed the synthesis of amorphous ultrathin MoCo_xO_y nanosheets with excellent OER catalytic performance, through an ion etching and pyrolysis assisted strategy. The incorporation of molybdate ions not only modifies the material architecture to generate two-dimensional layered nanosheet structures, but also regulates the local coordination environment and electronic structure of the cobalt oxide. The incorporation of molybdenum introduces abundant vacancies and oxygen adsorbed species. Besides, the amorphous nanosheet architecture of the material favors the presence of surface defects and coordinatively unsaturated sites, boosting the exposure of active sites and further improving catalytic activity. Finally, using several pieces of evidence we revealed the incorporation of molybdenum to enable a LOM, which is in part responsible for the excellent OER performance obtained.

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Chapter 3

Sulfate-Decorated Amorphous-Crystalline Cobalt-Iron Oxide Nanosheets to Enhance O-O Coupling in the Oxygen Evolution Reaction

3.1 Abstract

The development of efficient and low-cost electrocatalysts for the oxygen evolution reaction (OER) is critical to improving the efficiency of several electrochemical energy conversion and storage devices. Herein, we detail the synthesis of cobalt-iron oxide nanosheets containing controlled amounts of well-anchored SO_4^{2-} anionic groups ($\text{CoFe}_x\text{O}_y\text{-SO}_4$). We use a cobalt-based zeolitic imidazolate framework (ZIF-67) as the structural template and cobalt source, and Mohr's salt ($(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$) as the source of iron and sulfate. When combining the ZIF-67 with ammonium iron sulfate, the protons produced by the ammonium ion hydrolysis ($\text{NH}_4^+ + \text{H}_2\text{O} = \text{NH}_3 \cdot \text{H}_2\text{O} + \text{H}^+$) etch the ZIF-67, dissociating its polyhedron structure, and form porous assemblies of two-dimensional nanostructures through a diffusion-controlled process. At the same time, iron ions partially replace cobalt within the structure and SO_4^{2-} ions are anchored on the material surface by exchange with organic ligands. As a result, ultrathin $\text{CoFe}_x\text{O}_y\text{-SO}_4$ nanosheets are obtained. The proposed synthetic procedure enables controlling the amount of Fe and SO_4 ions and to analyze the effect of each element on the electrocatalytic activity. The optimized $\text{CoFe}_x\text{O}_y\text{-SO}_4$ material displays superior OER electrocatalytic performance with an overpotential of 268 mV at 10 mA cm^{-2} , a Tafel slope of 46.5 mV dec^{-1} , and excellent stability during 62 h. This excellent performance is correlated to the material structural and chemical parameters. The assembled nanosheet structure provides a large electrochemically active surface area, a high density of reaction sites, and fast electron transportation. Meanwhile, the introduction of iron increases the electrical conductivity of the catalysts and provide fast reaction sites with optimum bond energy and spin state for the adsorption of OER intermediates. The presence of sulfate ions at the catalyst surface modifies the electronic energy level of active sites, regulates

the adsorption of intermediates to reduce the OER overpotential, and promotes the surface charge transfer, which accelerates the formation of oxygenated intermediates. Overall, the present work not only presents a highly efficient OER electrocatalyst but also demonstrates the introduction of non-metallic anionic groups as an excellent strategy to promote electrocatalytic activity in energy conversion technologies.

3.2 Introduction

The oxygen evolution reaction (OER) is the limiting step in various electrochemical energy technologies, including water electrolysis, regenerative fuel cells, electrochemical CO₂ reduction, and metal-air batteries.¹⁻³ OER is characterized by slow kinetics and high overpotentials associated with the need to transfer four electrons to generate each O₂ molecule, the formation of multiple intermediates (*OH, *O, and *OOH) and the demanding O–O bond realization.⁴⁻⁷ Owing to its high technological and socio-economic interest, numerous classes of materials have been optimized and tested as OER electrocatalysts. Among them, transition metal nitrides, phosphides and chalcogenides have been recently reported as particularly active OER catalysts, reaching similar and even better performance than benchmark IrO₂ and RuO₂ electrocatalysts in alkaline electrolyte.⁸⁻¹⁰ Nevertheless, we and others have demonstrated the chemical conversion and restructuration of the surface of metal nitrides, phosphides or chalcogenides (MX; X=N, P, S, Se) to metal oxide (MO), hydroxide (MOH) and mainly oxohydroxide (MOOH) during OER in alkaline media.¹¹⁻¹³ Thus the properties of the derived oxide, hydroxide or oxohydroxide surfaces has been the focus of several recent studies. However, during this surface reconstruction, the surface anions are simultaneously oxidized to nitrates (NO₃⁻), phosphates (PO₄³⁻), sulfates (SO₄²⁻), and selenates (SeO₄²⁻),¹⁴⁻¹⁶ which presence on the catalyst surface and role in the electrocatalytic reaction have been largely overlooked.

Few recent works have demonstrated the presence of nonmetallic anionic groups as key to boosting water oxidation activity.¹⁷⁻²¹ Accordingly, the engineering of oxides containing controlled amounts of these groups could be a promising strategy to improve the surface reaction kinetics.^{21,22} Nevertheless, the introduction of nonmetallic anionic groups through the indirect conversion of non-metallic elements leads to uncontrolled amounts of this impurity, which limits the optimization of the catalyst. On the other hand, the introduction of anionic groups a posteriori, through surface adsorption, results in a

weak chemical interaction that limits effectiveness and stability of the resultant materials.^{14,17} Thus, an approach for the direct incorporation of controlled amounts of anionic groups that enable a strong bonding between anions and metal atoms is intensely pursued as it is expected to remarkably facilitate water oxidation.

On the other hand, some amorphous catalysts present improved OER performance over their crystalline counterpart.^{23,24} Amorphous catalysts offer higher flexibility in terms of composition and atomic arrangement, which allows for more facile incorporation of a wide range and concentration of extrinsic dopants.^{25,26} A higher variety of oxidation states of multivalence metals is also possible in amorphous structures, which contain more unsaturated coordination spheres. Amorphous oxides are also generally characterized by less strongly bond oxygen ions compared with crystalline materials, which could facilitate an efficient lattice oxygen-mediated OER mechanism.²⁷⁻³¹ As a drawback, the charge transfer kinetics of amorphous catalysts is limited by their lower electrical conductivity.³²⁻³⁵ Therefore, to rationally design and engineer optimized electrocatalysts, the balance between amorphous and crystalline phases is an additional key parameter to be tuned.

Herein, we introduce controlled amounts of SO_4^{2-} anionic groups into partially amorphous CoFeO_x by a facile ion exchange and etching method. We thoroughly analyze the structural and chemical properties of the produced material and correlate them with their electrocatalytic performance. Exploiting the control possibilities provided by the synthesis method and taking into account the uncovered property-performance correlations, the electrocatalyst is optimized to reach outstanding OER performances.

3.3 Experimental Section

3.3.1 Chemicals

Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99.9%), ammonium iron(II) sulfate hexahydrate (Mohr's salt, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, 99%), ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$, 99%), iron (II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$, 99%), potassium hydroxide (KOH, 85%), and 2-methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$, 99%) were purchased from Acros Organics. Iridium(IV) oxide (IrO_2 , 99.9% metal basis) and Nafion (5 wt% in a mixture of low aliphatic alcohols and water) were obtained from Sigma-Aldrich. Methanol, ethanol and isopropanol were of analytical grade and obtained from various sources. Milli-Q water

was obtained from a Purelab flex from Elga. All chemicals were used as received, without further purification.

3.3.2 Zeolitic imidazolate framework (ZIF-67)

ZIF-67 was obtained from a modified procedure based on previous reports [15, 37]. Briefly, 0.87 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 30 mL methanol. Subsequently, the clear solution obtained was poured into 30 mL methanol containing 1.97 g 2-methylimidazole under vigorous stirring. The obtained mixture was incubated for 24 h at room temperature. Purple precipitates were collected by centrifugation, washed with methanol at least three times, and finally dried at 60 °C overnight.

3.3.3 Synthesis of CoFe-MOFs

120 mg of as-prepared ZIF-67 powder was ultrasonically re-dispersed in 20 mL ethanol. This dispersion was poured into 100 mL of an aqueous solution containing 100 mg, 200 mg or 400 mg $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ under continuous magnetic stirring. The mixture was then stirred vigorously for 12 hours at room temperature. Precipitates were collected by centrifugation, washed with water at least three times, and finally freeze-dried overnight. The obtained products were labelled as CoFe-MOFs-100, CoFe-MOFs-200 and CoFe-MOFs-400. To study the effect of the reaction time, CoFe-MOF-200 samples with different reaction times were also obtained by stirring ZIF-67 powder into a 100 mL aqueous solution containing 200 mg ammonium iron(II) sulfate for 1 hour or 3 hours. The effect of the Fe precursor and the SO_4^{2-} ions were studied by replacing $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ with the same molar amount FeCl_2 or $(\text{NH}_4)_2\text{SO}_4$. These samples were labelled as FeCl_2 -ZIF-67 and $(\text{NH}_4)_2\text{SO}_4$ -ZIF-67.

3.3.4 Synthesis of reference Co_3O_4 nanocrystals and amorphous CoFe_xO_y nanosheets.

ZIF-67 and CoFe MOFs were annealed in a muffle furnace at 350 °C for 2 hours with a heating rate of 3 °C min⁻¹ under air atmosphere. The black products obtained from the annealing of ZIF-67 and the different CoFe MOFs were denoted as Co_3O_4 and CoFe_xO_y - SO_4 -100, CoFe_xO_y - SO_4 -200, CoFe_xO_y - SO_4 -400, CoFe_xO_y -Cl and Co_3O_4 - SO_4 , respectively. The effect of the annealing temperature was studied by annealing the CoFe-MOFs-200 at 450 °C and 550 °C for 2 hours in air. The obtained samples were named

CoFe_xO_y-SO₄-450 °C and CoFe_xO_y-SO₄-550 °C, respectively. Table S1 displays the complete list of samples produced and analyzed in this work.

Table S1. Complete list of samples produced and characterized, including name, precursors and processing conditions.

Sample name	MOF	Fe precursor	Fe precursor amount (mg)	Stirring time (h)	Annealing temperature (°C)
ZIF-67	ZIF-67	-	-	-	-
(NH ₄) ₂ SO ₄ -ZIF-67	ZIF-67				
Co-Fe MOF-100	ZIF-67	(NH ₄) ₂ Fe(SO ₄) ₂ ·6H ₂ O	100	12	-
Co-Fe MOF-200	ZIF-67	(NH ₄) ₂ Fe(SO ₄) ₂ ·6H ₂ O	200	12	-
Co-Fe MOF-200-1h	ZIF-67	(NH ₄) ₂ Fe(SO ₄) ₂ ·6H ₂ O	200	1	-
Co-Fe MOF-200-3h	ZIF-67	(NH ₄) ₂ Fe(SO ₄) ₂ ·6H ₂ O	200	3	-
Co-Fe MOF-400	ZIF-67	(NH ₄) ₂ Fe(SO ₄) ₂ ·6H ₂ O	400	12	-
FeCl ₂ -ZIF-67	ZIF-67	FeCl ₂		12	
Co ₃ O ₄	ZIF-67	-	-	-	350
Co ₃ O ₄ -SO ₄	ZIF-67	(NH ₄) ₂ SO ₄		12	350
CoFe _x O _y -SO ₄ -100	ZIF-67	(NH ₄) ₂ Fe(SO ₄) ₂ ·6H ₂ O	100	12	350
CoFe _x O _y -SO ₄ -200	ZIF-67	(NH ₄) ₂ Fe(SO ₄) ₂ ·6H ₂ O	200	12	350
CoFe _x O _y -SO ₄ -450°C	ZIF-67	(NH ₄) ₂ Fe(SO ₄) ₂ ·6H ₂ O	200	12	450
CoFe _x O _y -SO ₄ -550°C	ZIF-67	(NH ₄) ₂ Fe(SO ₄) ₂ ·6H ₂ O	200	12	550
CoFe _x O _y -SO ₄ -1h	ZIF-67	(NH ₄) ₂ Fe(SO ₄) ₂ ·6H ₂ O	200	1	350
CoFe _x O _y -SO ₄ -3h	ZIF-67	(NH ₄) ₂ Fe(SO ₄) ₂ ·6H ₂ O	200	3	350
CoFe _x O _y -SO ₄ -400	ZIF-67	(NH ₄) ₂ Fe(SO ₄) ₂ ·6H ₂ O	400	12	350
CoFe _x O _y -Cl	ZIF-67	FeCl ₂	140	12	350

3.3.5 Sample Characterization

Powder Powder X-ray diffraction (XRD) patterns were obtained on a Bruker AXS D8 Advance X-ray diffractometer with Ni-filtered (2 µm thickness) Cu-Kα radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 mA and 40 kV. Scanning electron microscopy (SEM) analysis was conducted with a Zeiss Auriga microscope (Carl Zeiss, Jena, Germany) equipped with an energy-dispersive X-ray spectroscopy (EDX) detector operating at 20 kV. Transmission electron microscopy (TEM) images were carried out with a Zeiss Libra 120 (Carl Zeiss, Jena, Germany) operating at 120 kV. High-resolution TEM (HRTEM) analysis images were obtained using a field emission gun FEI™ Tecnai F20 microscope at 200 kV with a point-to-point resolution of 0.19 nm. High angle annular dark-field scanning transmission electron microscope (HAADF-STEM) was combined with electron energy loss spectroscopy (EELS) in the Tecnai F20 with a Gatan Quantum filter. X-ray photoelectron spectroscopy (XPS) was analyzed on a SPECS system (SPECS GmbH, Berlin, Germany) equipped with an Al anode XR50 source operating at 150 W and a Phoibos 150 MCD-9 detector. The pressure in the analysis chamber was kept below 10^{-7} Pa. Data processing was performed with the Casa XPS program (Casa Software Ltd.,

UK). Binding energy (BE) values were centered by using the C 1s peak at 284.8 eV. Thermogravimetric analyses (TGA) were carried out in air atmosphere in the temperature range from 50 to 700 °C with a ramp of 5 °C min⁻¹ using a PerkinElmer Diamond TG/DTA Instruments (PerkinElmer, Waltham, MA).

3.3.6 Electrode preparation and electrochemical measurements

The working electrode was prepared as follows: 5 mg of as-prepared catalyst was dispersed in a mixture solution of 750 µL isopropanol and 220 µL deionized water. Then 30 µL Nafion (5 wt %) was added and the solution was sonicated for at least 30 min until forming a homogeneous ink. 5 µL of the fresh catalyst ink was dropped onto a glassy carbon (GC, 3 mm in diameter) electrode and naturally dried in air. The loading capacity was 0.145 mg cm⁻². All electrochemical measurements were performed at room temperature on a model CHI760E electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China) in a standard three-electrode cell, with the fabricated GC electrode as working electrode, a graphite rod as counter electrode and a Hg/HgO (1.0 M KOH) reference electrode. Linear sweep voltammetry (LSV) was conducted at a scan rate of 5 mV s⁻¹ from 0 to 1.0 V (vs. Hg/HgO) in O₂-saturated 1.0 M KOH electrolyte. All the presented data were corrected with 90% iR-compensation. Electrical impedance spectroscopy (EIS) was measured in a frequency range from 100 kHz to 0.01 Hz at 5 mV and recorded at 1.55 V. The electrochemical double-layer capacitance (C_{dl}) curves of catalysts were measured by cyclic voltammetry in a non-Faradaic region (0.90–1.00 V vs. RHE) at varied scan rates of 20 to 200 mV s⁻¹ based on the following equation: $C_{dl} = \Delta j / v$, where Δj ($\Delta j = (j_a - j_c)/2$) and v are the current density (at 0.95 V, mA cm⁻²) and scan rate (mV s⁻¹), respectively. The long-term durability was tested using chronopotentiometry (CP) at a constant current density of 10 mA cm⁻² for 60 h without iR compensation and LSVs after continuous cyclic voltammetry tests (1.3 V to 1.7 V) for 2000 cycles at 0.2 V s⁻¹. In-situ Raman spectra were collected after different CV cycles (1.3 to 1.7 V at a scan rate of 0.1 V s⁻¹) on an Xplora Plus Raman microscope (Horiba, France) with a 532 nm excitation wavelength. All obtained potential (vs. Hg/HgO) was converted to the reversible hydrogen electrode (RHE) according to Nernst equation: $E_{RHE} = E_{Hg/HgO} + 0.059 \text{ pH} + E^{\ominus}_{Hg/HgO}$, ($E^{\ominus}_{Hg/HgO} = 0.098 \text{ V}$). All corresponding current densities were normalized using the uniform geometrical area of the GCE (0.07 cm²). For all testing, a flow of O₂ was used to purge the electrolyte to guarantee the O₂/H₂O equilibrium at 1.23

V. The over-potentials (η) at 10 mA cm^{-2} were calculated as follows: $\eta = E \text{ (vs. RHE)} - 1.23$, considering the $\text{O}_2/\text{H}_2\text{O}$ equilibrium at 1.23 V.

3.4 Results and discussion

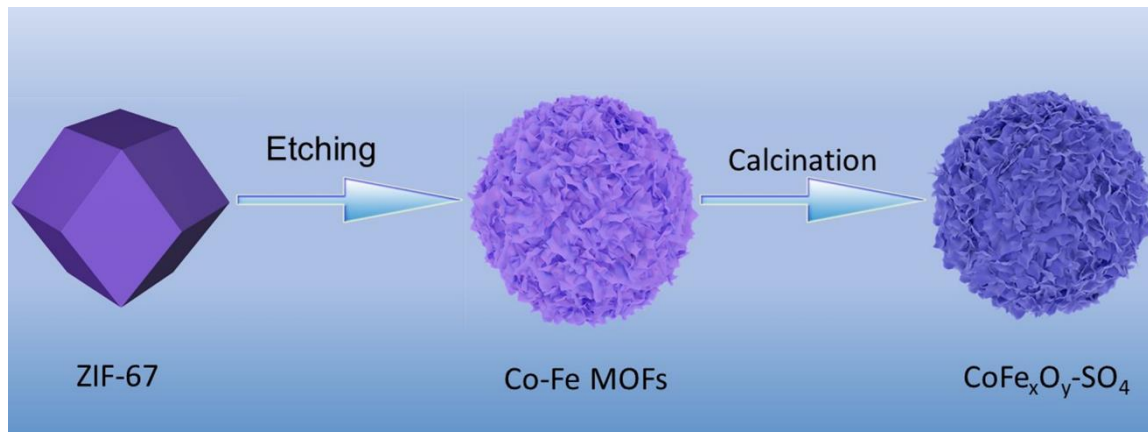


Figure 3.1. Schematic illustration of the $\text{CoFe}_x\text{O}_y\text{-SO}_4$ synthesis process.

Figure 3.1 schematically displays the three-step process used to produce assembled $\text{CoFe}_x\text{O}_y\text{-SO}_4$ nanosheets. First, a crystalline cobalt-based zeolitic imidazolate framework (ZIF-67) was synthesized to be used as structural template and cobalt source.^{36, 37} Subsequently, ZIF-67 was reacted with $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ to etch the structure and partially exchange the metal (see the Experimental section for details). In this process, the protons produced by the ammonium ion hydrolysis ($\text{NH}_4^+ + \text{H}_2\text{O} = \text{NH}_3 \cdot \text{H}_2\text{O} + \text{H}^+$) etch the ZIF-67, dissociating its polyhedron structure. We hypothesize that iron ions partially replace cobalt within the structure, and that using an iron sulfate salt, SO_4^{2-} ions are anchored on the material surface by exchange with organic ligands.

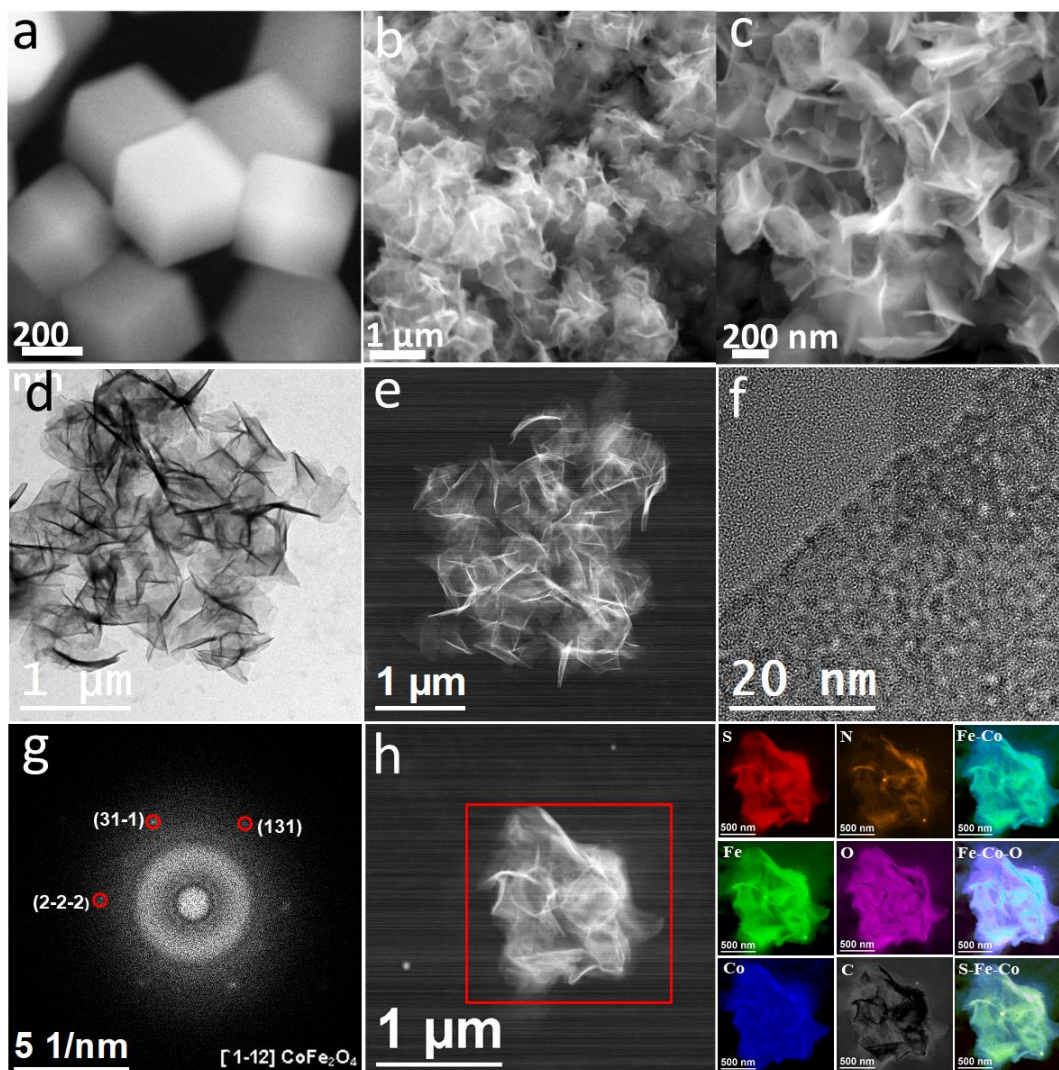


Figure 3.2. SEM images of a) ZIF-67, b) CoFe MOFs, and c) $\text{CoFe}_x\text{O}_y\text{-SO}_4$. d) TEM, e) HAADF image, f) HRTEM image, g) corresponding FFT spectrum and h) EELS chemical composition maps of $\text{CoFe}_x\text{O}_y\text{-100}$ nanosheets. EELS chemical composition maps were obtained from the red squared area of the STEM micrograph. Individual S $L_{2,3}$ -edges at 165 eV (red), Fe $L_{2,3}$ -edges at 708 eV (green), Co $L_{2,3}$ -edges at 779 eV (blue), N K-edge at 401 eV (orange), O K-edge at 532 eV (pink) and C K-edge at 284 eV (grey) and composites of Fe-Co, Fe-Co-O and S-Fe-Co.

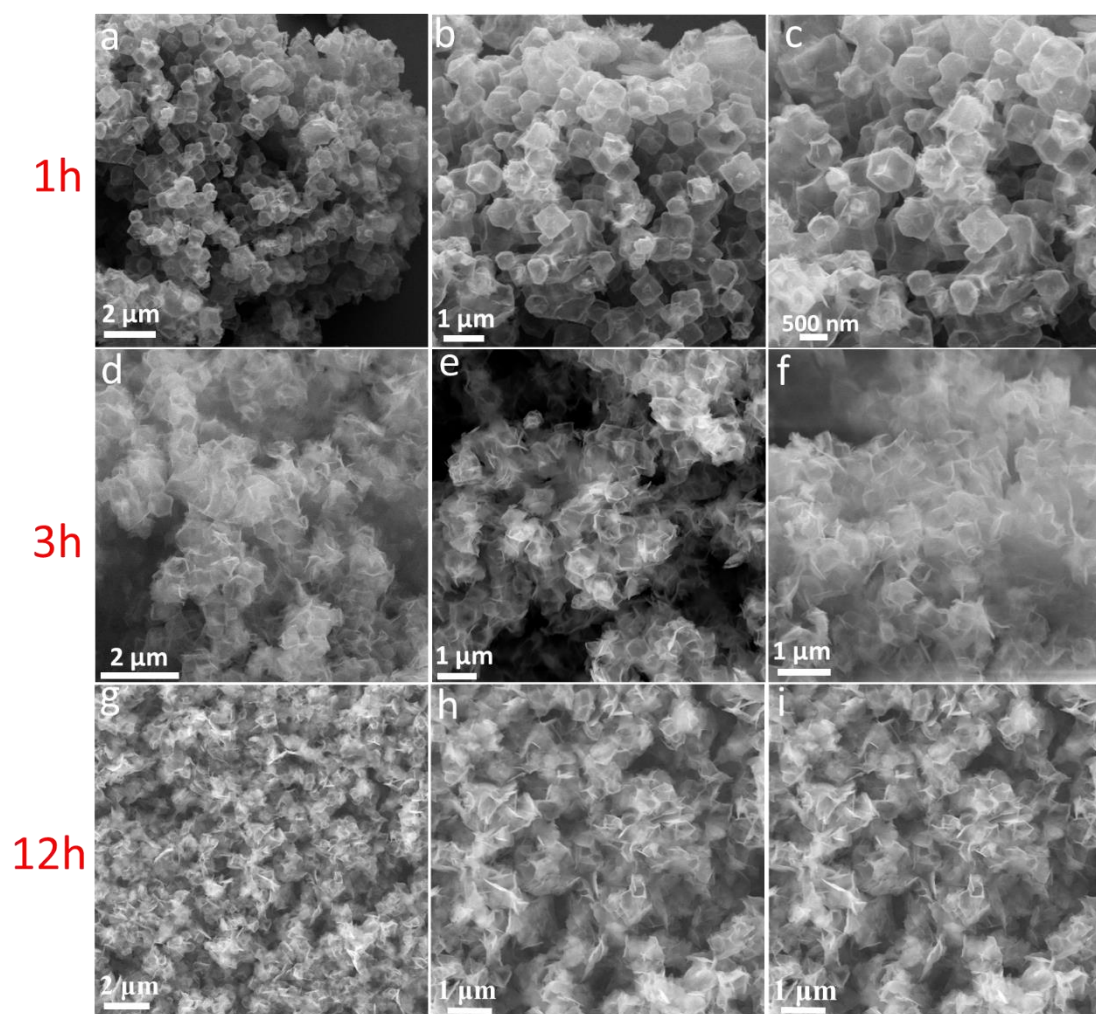


Figure 3.3. SEM images of a-c) CoFe_xO_y-SO₄-1h, d-f) CoFe_xO_y-SO₄-3h, g-i) CoFe_xO_y-SO₄-12h.

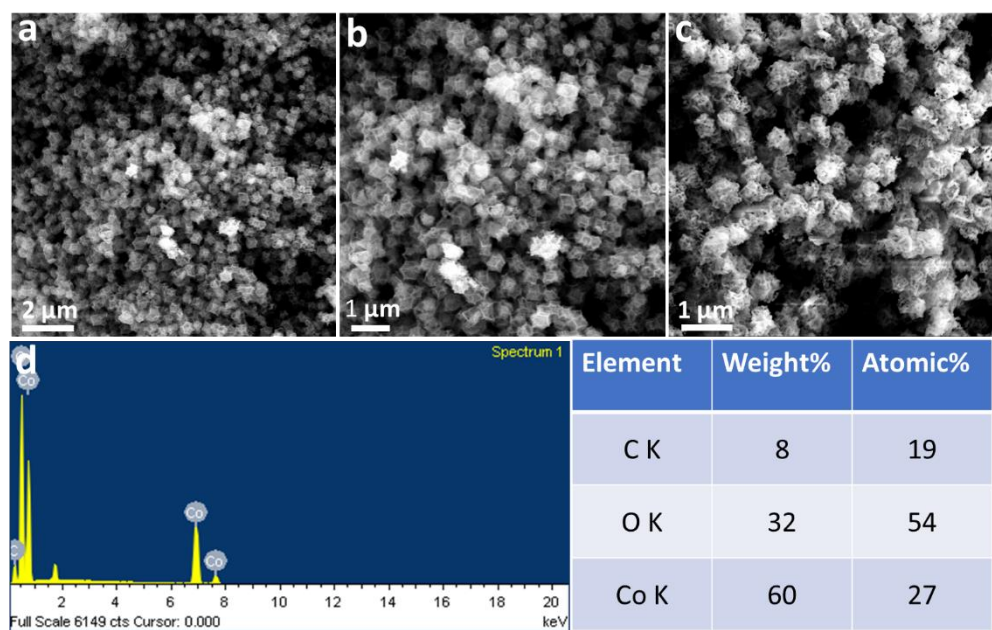


Figure 3.4. (a-c) SEM images and (d) EDX spectrum of Co_3O_4

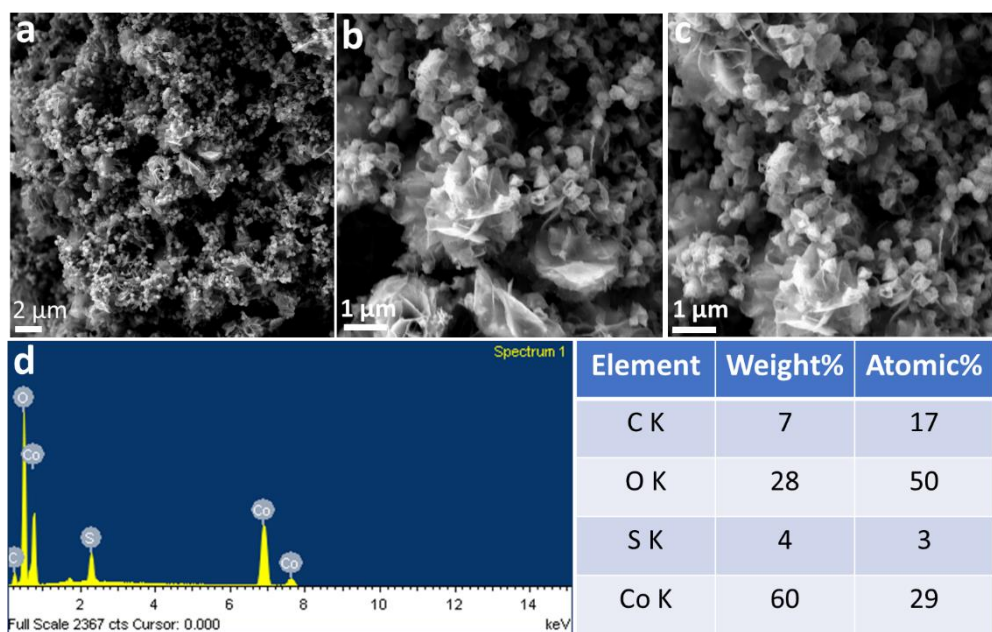


Figure 3.5. (a-c) SEM images and (d) EDX spectrum of $\text{Co}_3\text{O}_4\text{-SO}_4$

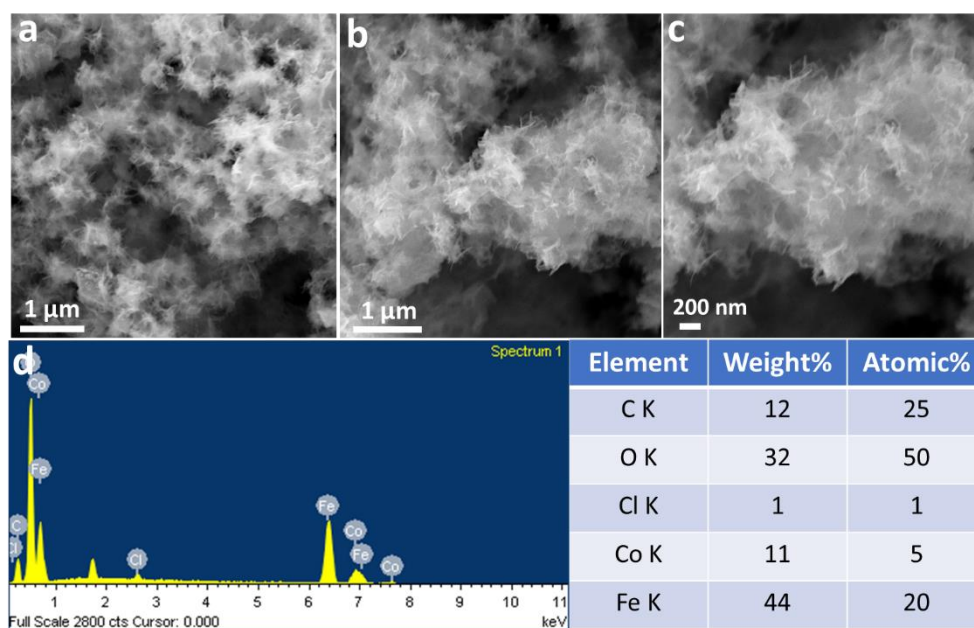


Figure 3.6. (a-c) SEM images and (d) EDX spectrum of $\text{CoFe}_x\text{O}_y\text{-Cl}$.

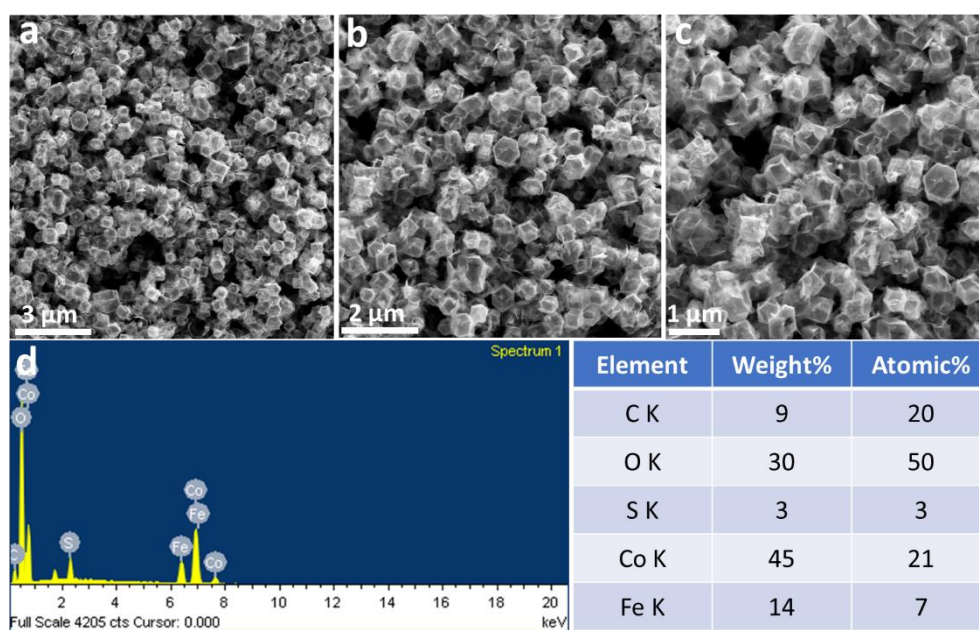


Figure 3.7. (a-c) SEM images and (d) EDX spectrum of $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-100-350}^\circ\text{C}$.

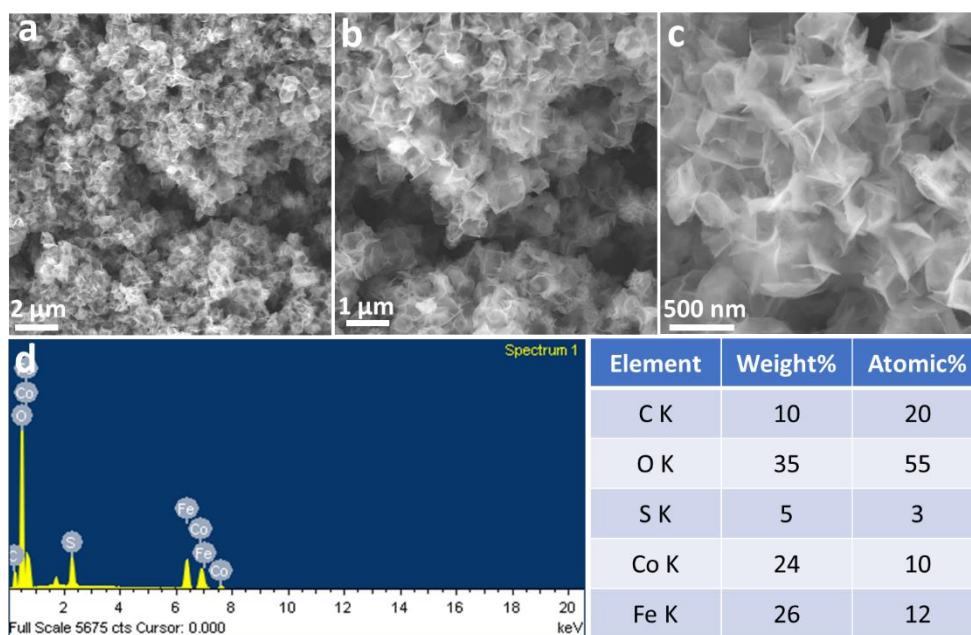


Figure 3.8. (a-c) SEM images and (d) EDX spectrum of $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200-350}^\circ\text{C}$.

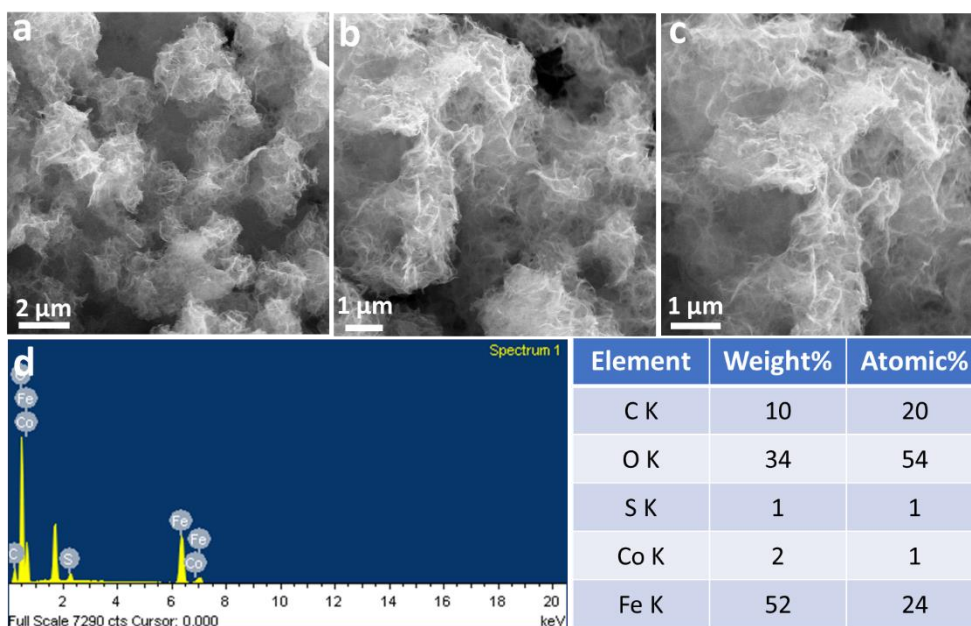


Figure 3.9. (a-c) SEM images and (d) EDX spectrum of $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-400-350}^\circ\text{C}$.

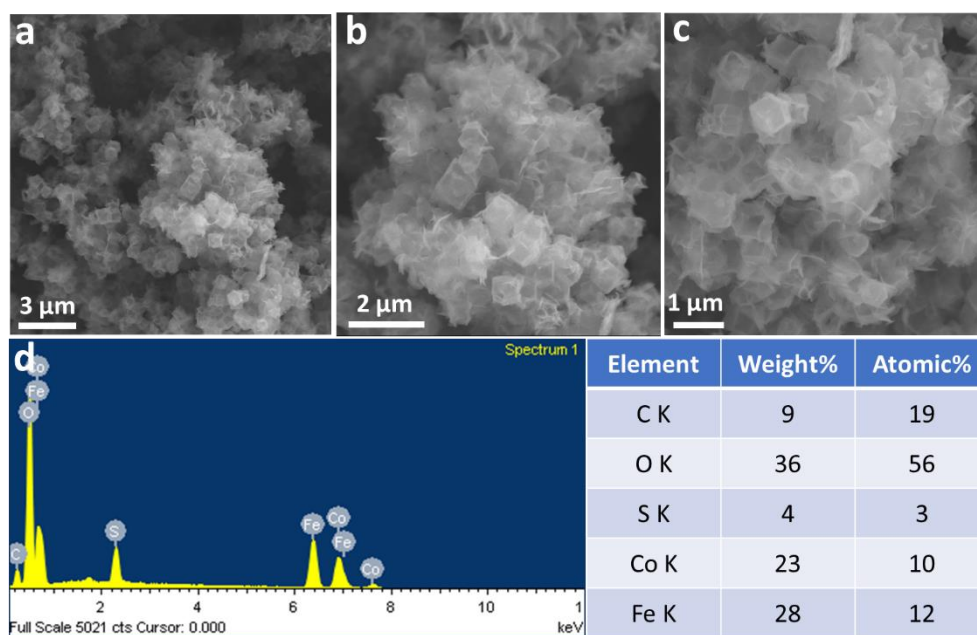


Figure 3.10. (a-c) SEM images and (d) EDX spectrum of $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200-450}^\circ\text{C}$.

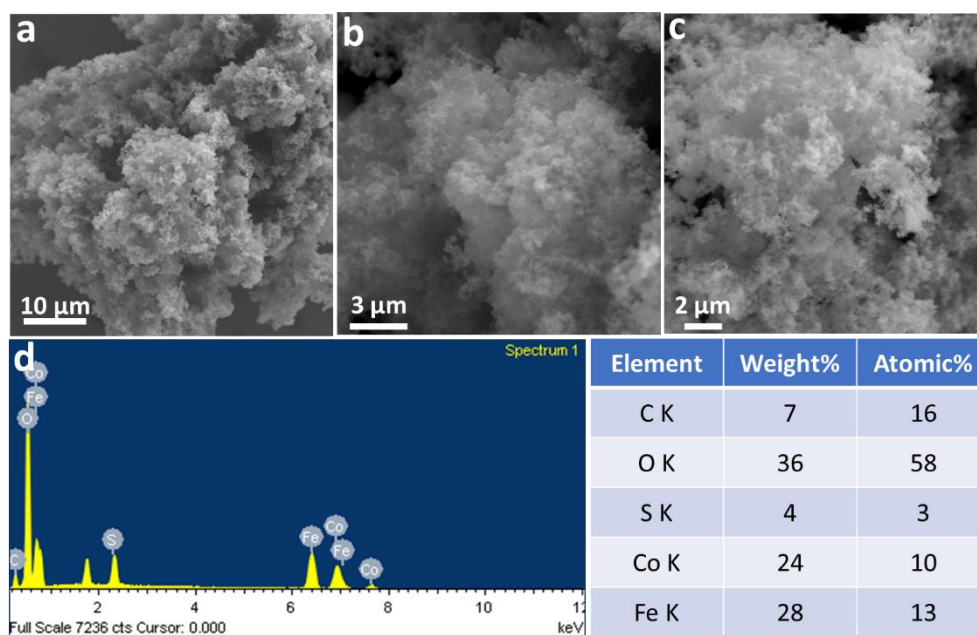


Figure 3.11. (a-c) SEM images and (d) EDX spectrum of $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200-550}^\circ\text{C}$.

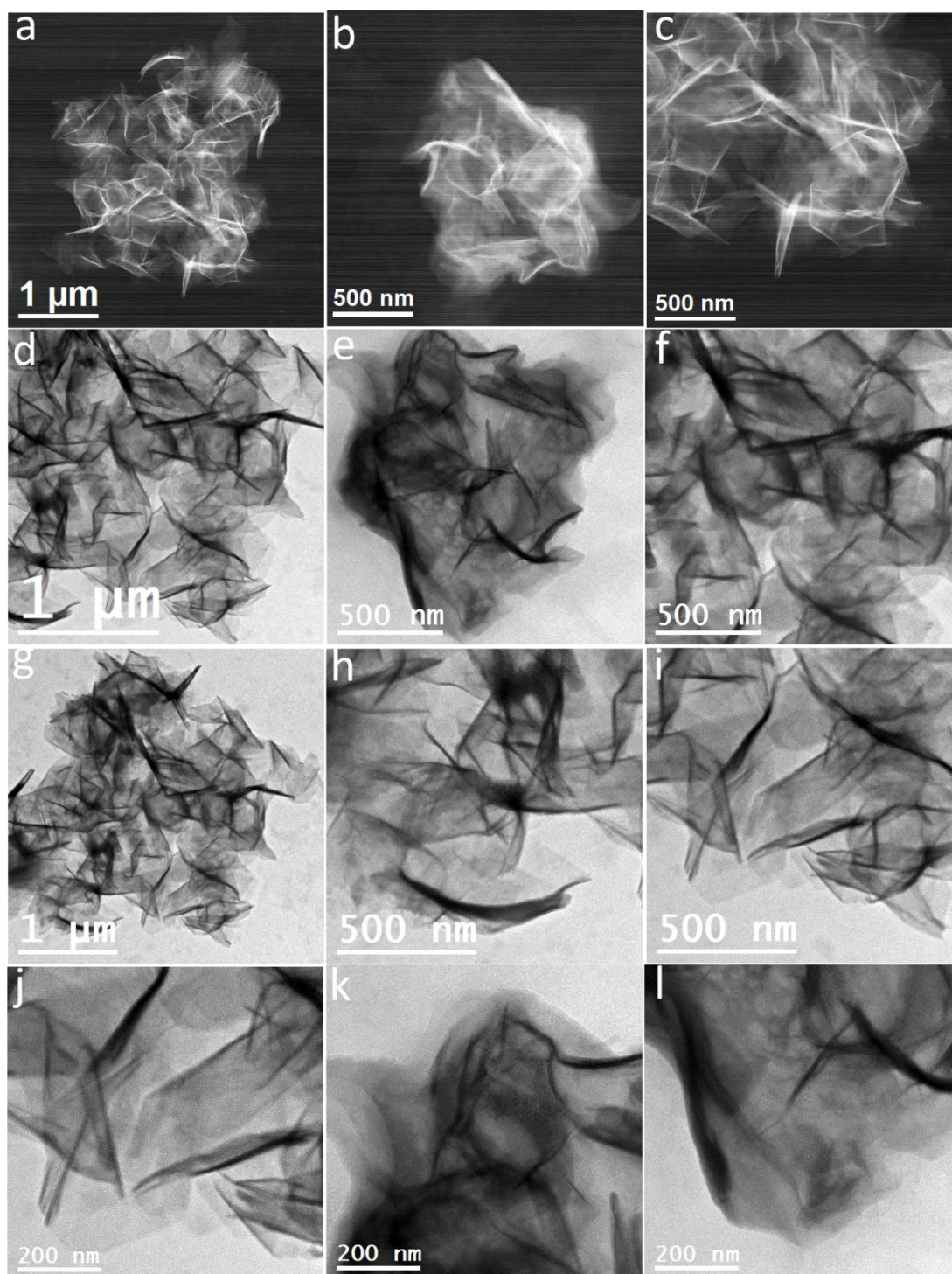


Figure 3.12. (a-c) STEM and (d-l) TEM images of $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$.

Figure 3.2a displays a representative SEM image of the ZIF-67 template, which shows a smooth rhombic dodecahedron morphology with a uniform particle size of about 350 nm. The ZIF-67 template is highly crystalline, as observed by powder XRD analysis (Figure 3.13). Upon reaction with the Mohr's salt, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, a different structure progressively expands around the gradually disappearing ZIF-67 template (Figure 3.2b). Eventually, after 12 h reaction, the dodecahedron template has fully disappeared and only a porous nanosheet structure is observed (Figure 3.3). XRD analyses revealed the crystal structure of ZIF-67 to be lost after just 3 h of ion etching and exchange (Figures 3.13a and 3.14a).

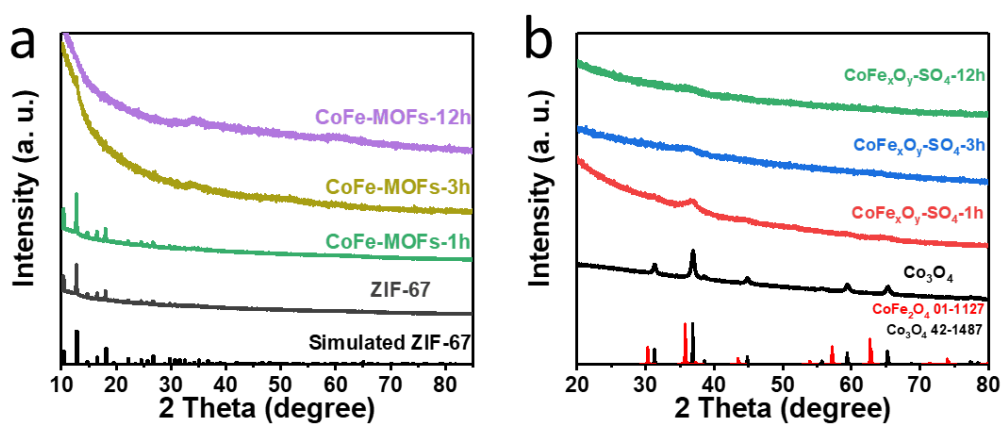


Figure 3.13. XRD patterns of (a) CoFe-MOFs and (b) CoFe_xO_y-SO₄ of different reaction time (1h, 3h, 12h).

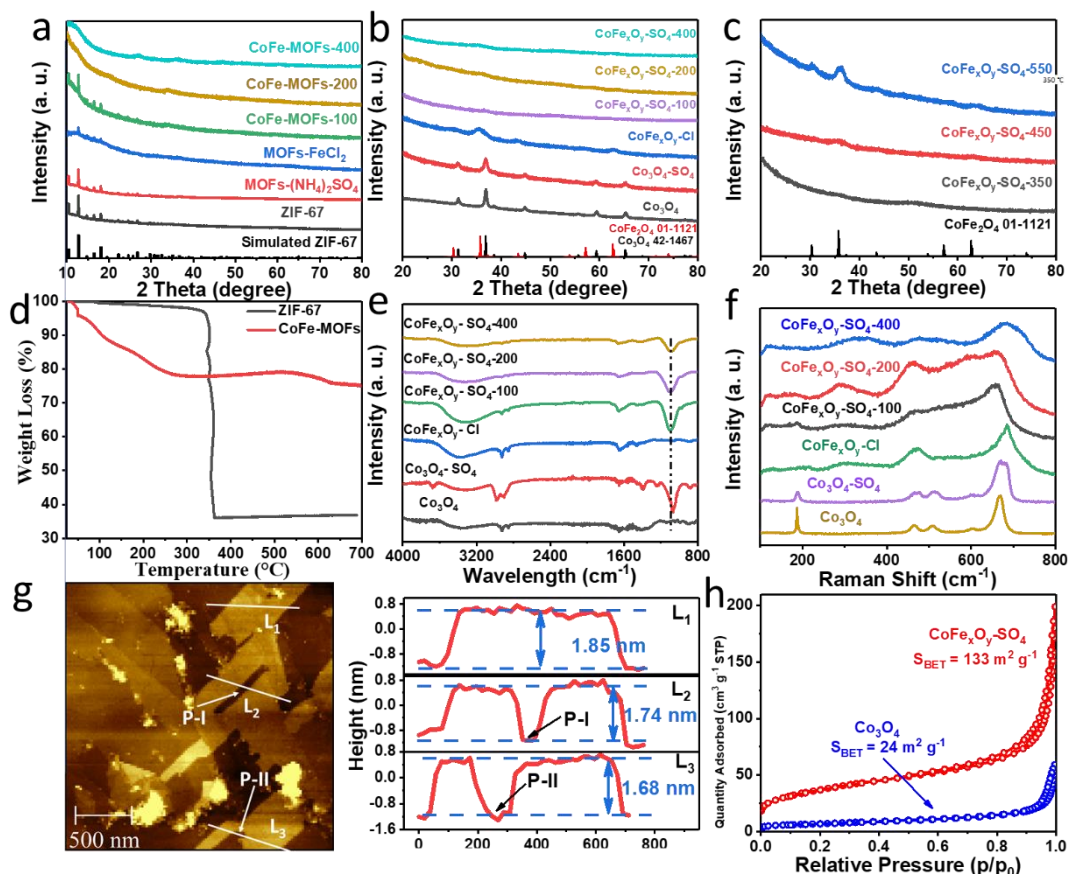


Figure 3.14. (a-c) XRD pattern of a) initial MOFs, b) Co_3O_4 , $\text{Co}_3\text{O}_4\text{-SO}_4$, $\text{CoFe}_x\text{O}_y\text{-Cl}$ and $\text{CoFe}_x\text{O}_y\text{-SO}_4$ with different compositions, and c) $\text{CoFe}_x\text{O}_y\text{-200}$ after annealing at different temperatures. d) TGA curves under air atmosphere of ZIF-67 and CoFe MOFs. e) FTIR spectra and f) Raman spectra of Co_3O_4 , $\text{CoO}_x\text{-SO}_4$, $\text{CoFe}_x\text{O}_y\text{-Cl}$ and $\text{CoFe}_x\text{O}_y\text{-SO}_4$. g) AFM images and the corresponding thickness measurement data of $\text{CoFe}_x\text{O}_y\text{-200}$. h) N_2 adsorption-desorption isotherms for $\text{CoFe}_x\text{O}_y\text{-200}$.

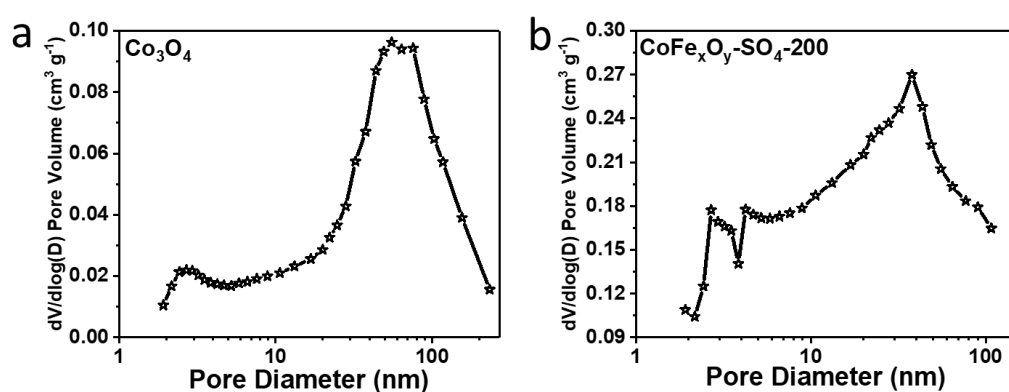


Figure 3.15. Pore size distribution plot for Co_3O_4 and $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$.

ZIF-67 and CoFe MOFs were annealed in air to remove organic ligands. TGA displayed weight loss steps at 280 °C and 350 °C for CoFe-MOFs and ZIF-67,

respectively. Thus, 350°C was selected as the annealing temperature to remove unstable organic ligands while minimizing the material crystallization and carbon loss, which will contribute to promoting the electrical conductivity of the final material. Figure 2c-e shows SEM, TEM and STEM images of the ultrathin nanosheets with wrinkled structure obtained after annealing the CoFe-MOF at 350 °C in an air atmosphere. HAADF-STEM and EELS mapping (Figure 3.2h, 3.17) showed C, N, O, S, Co and Fe elements to be homogeneously distributed throughout the nanosheets.

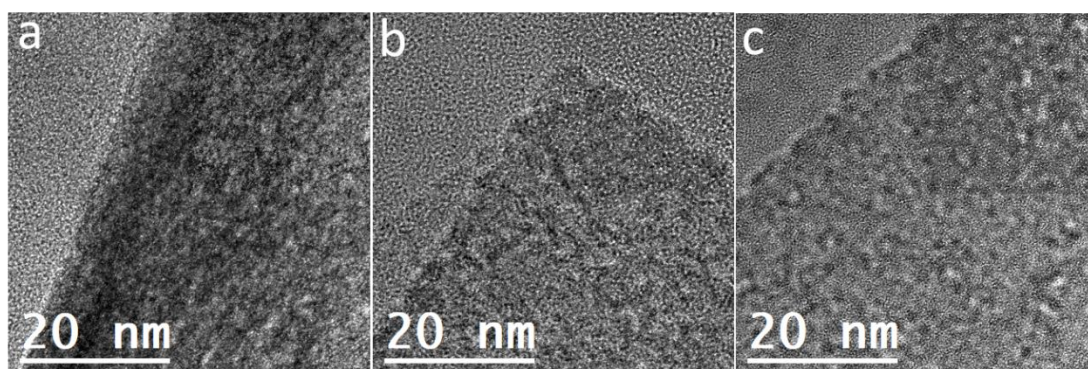


Figure 3.16. (a-c) HRTEM images of CoFe_xO_y-SO₄-200.

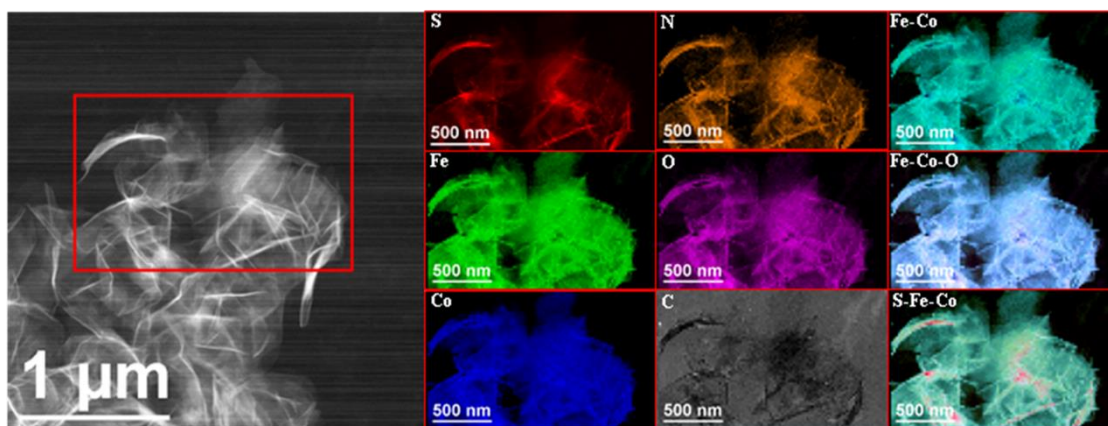


Figure 3.17. EELS chemical composition maps of CoFe_xO_y-SO₄-200 obtained from the red squared area of the STEM micrograph. Individual S L_{2,3}-edges at 165 eV (red), Fe L_{2,3}-edges at 708 eV (green), Co L_{2,3}-edges at 779 eV (blue), N K-edge at 401 eV (orange), O K-edge at 532 eV (pink) and C K-edge at 284 eV (grey) and composites of Fe-Co, Fe-Co-O and S-Fe-Co.

The material annealed at 350 °C presented an amorphous structure according to XRD patterns (Figure 3.14). HRTEM analysis confirmed the amorphous structure of CoFe_xO_y but detected some amorphous/crystalline interfaces (Figures 3.2f and 3.16). The corresponding indexed fast Fourier transform (FFT) crystallographic analyses confirmed the presence of a small amount of weakly crystalline CoFe₂O₄ (Figure 3.2g). Only when

increasing the annealing temperature to 450 °C and 550 °C the mostly amorphous CoFe_xO_y gradually transform into crystalline CoFe_2O_4 (JCPDS card No. 01-1121, Figure 3.14c).

Figures 3.14f and 3.14e display the Raman and FTIR spectra of the materials obtained from the annealing of ZIF-67 and CoFe-MOFs. Four obvious peaks were observed in the Raman spectrum of the annealed ZIF-67, at 185.5, 465.3, 506.6, and 670 cm^{-1} , which were associated with the F^1_{2g} , E^2_g , F^2_{2g} , and A^1_g phonon modes of crystalline Co_3O_4 . With the introduction of the iron sulfate, the peaks associated with the Co_3O_4 phase gradually weakened and disappeared. On the other hand, all the materials produced using the iron sulfate salt displayed an evident FTIR absorption peak at about 1100 cm^{-1} , which is a footprint of the presence of SO_4^{2-} ions.

The average thickness of the $\text{CoFe}_x\text{O}_y\text{-SO}_4$ nanosheets was about 1.75 nm, as determined by AFM (Figure 3.14g). This 2D nanostructure dramatically increases the percentage of surface unsaturated atoms, provides a high electroactive surface area, and at the same time facilitates the rapid diffusion of reactant.^{38, 39} From N_2 adsorption-desorption isotherms, the Brunauer-Emmett-Teller (BET) surface area of $\text{CoFe}_x\text{O}_y\text{-SO}_4$ was estimated at 133 $\text{m}^2 \text{g}^{-1}$, over a fivefold higher than that of Co_3O_4 (24 $\text{m}^2 \text{g}^{-1}$) obtained from the annealing of ZIF-67 (Figures 3.14h and 3.15). Besides, the Barrett-Joyner-Halenda (BJH) average pore size was 9 nm and 15 nm for $\text{CoFe}_x\text{O}_y\text{-SO}_4$ and Co_3O_4 , respectively.

To demonstrate the important role played by Fe ions in the formation of the $\text{CoFe}_x\text{O}_y\text{-SO}_4$ nanosheets, ZIF-67 templates were reacted with $(\text{NH}_4)_2\text{SO}_4$. Without iron, the protons produced by ammonium ions cannot completely etch and dissociate the ZIF-67 (Figure 3.5). Thus, the polyhedron morphology and its crystal structure are largely preserved (Figure 3.14a). On the other hand, to demonstrate the importance of selecting the proper salt, ZIF-67 was reacted with FeCl_2 . In this case, ion etching and dissociation were too thorough, and most of the cobalt in the catalyst was lost, as observed by EDX analysis (Figure 3.6). After annealing in air at 350 °C, the products obtained from the reaction with $(\text{NH}_4)_2\text{SO}_4$ and FeCl_2 displayed a good crystal structure, assigned to Co_3O_4 (JCPDS card No. 42-1467) and Fe_2O_3 (JCPDS card No. 73-0603), respectively (Figure 3.14b).

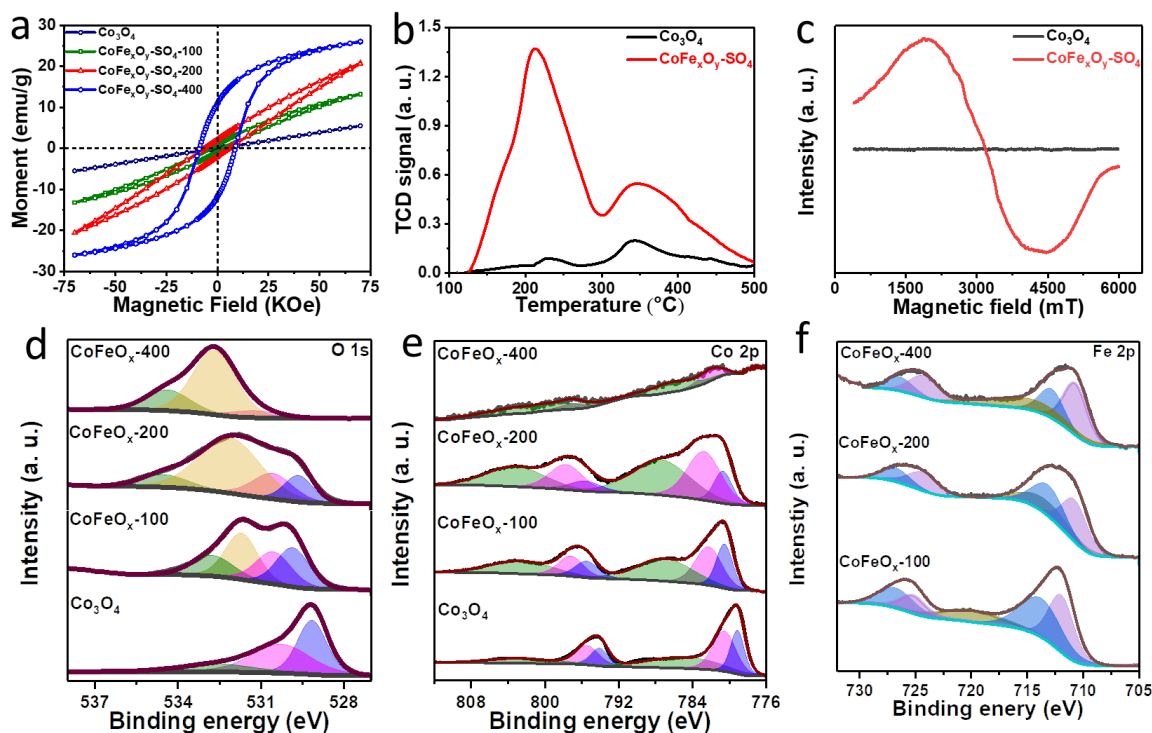


Figure 3.18. a) Magnetic hysteresis loops of CoFe_xO_y-100, 200, 400 and Co₃O₄ samples measured at 5 K. b - c) NH₃-TPD profiles EPR spectra of CoFe_xO_y-SO₄-200 and Co₃O₄. d-e) O 1s, Co 2p and Fe 2p_{3/2} XPS fitting of CoFe_xO_y-100, 200, 400 and Co₃O₄ samples.

The amount of Mohr's salt also played a critical role in controlling the morphology of the obtained material. Small amounts of (NH₄)₂Fe(SO₄)₂ (100 mg) did not generate enough protons to entirely consume the ZIF-67 template, thus resulting in hollow polyhedral nanocages with few surface wrinkles (Figure 3.7, 3.14b). Besides, the amount of (NH₄)₂Fe(SO₄)₂ also controlled the iron content of the final material, which is a key parameter to optimize its catalytic properties. In this direction, previous reports demonstrate the local spin state modification can have a large impact on the catalytic properties of the material by further filling the e_g orbital as well as increasing the overlap between the e_g orbital and OH⁻ adsorbate, which facilitates the formation of a σ bond between the high-valence Co and OH⁻ adsorbate^{14, 40, 41}. In our particular system, small amounts of (NH₄)₂Fe(SO₄)₂ (100 mg) resulted in highly Co-rich materials containing a very limited amount of iron. On the other hand, excess amounts of (NH₄)₂Fe(SO₄)₂ (400 mg) resulted in an almost full replacement of cobalt by iron ions (Figure 3.8). The change in the Fe content with the amount of (NH₄)₂Fe(SO₄)₂ salt used was also followed by characterizing the magnetic hysteresis loops of the samples. As displayed in Figures 3.18a

and 3.19, the Curie temperature, magnetization and coercive field increased with the amount of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ salt used, *i.e.* with the amount of Fe within the structure.

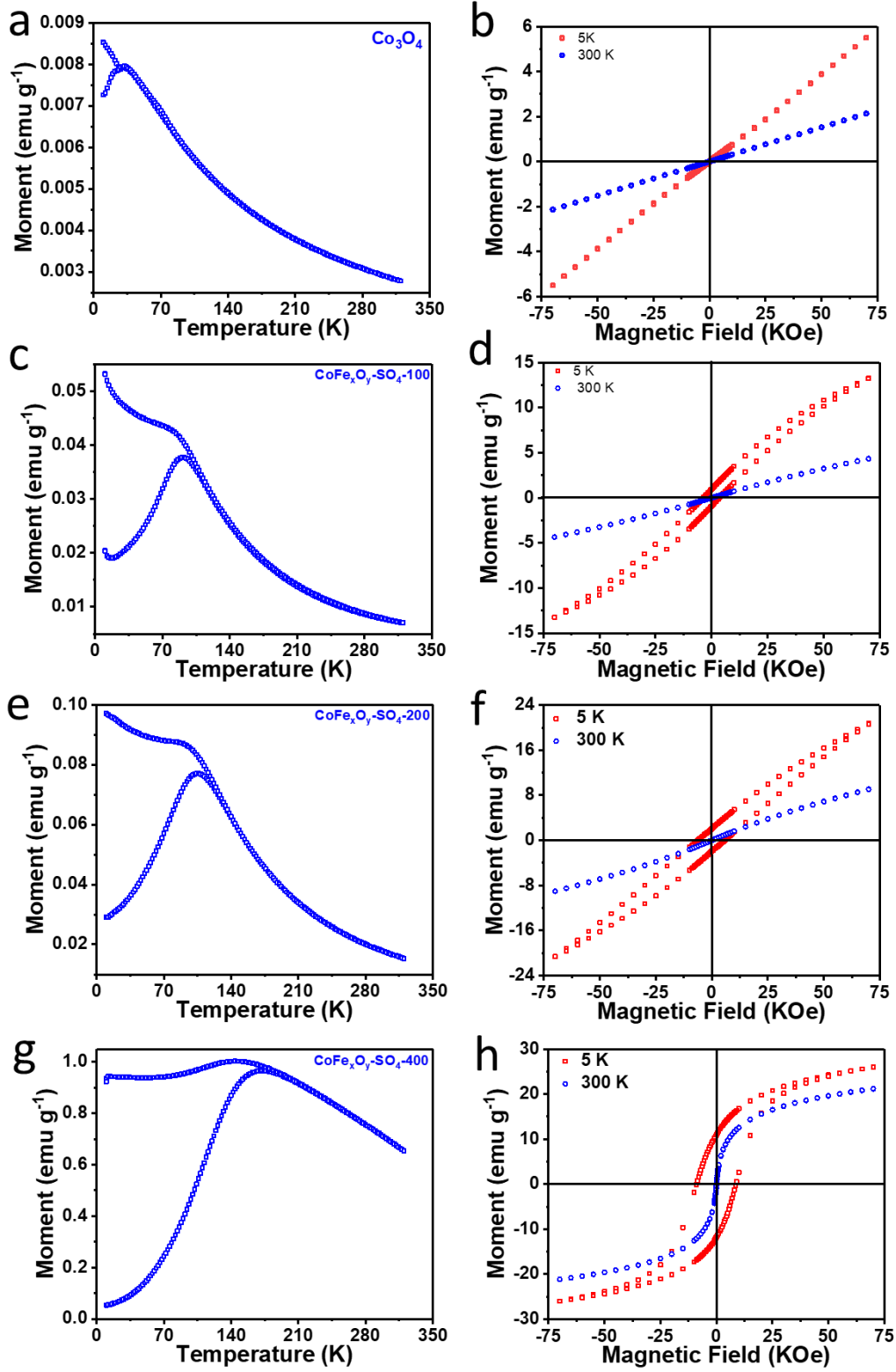


Figure 3.19. (a, c, e, g) Field cooled and zero field cooled magnetization curves of Co_3O_4 and $\text{CoFe}_x\text{O}_y\text{-SO}_4$ -100, 200, 400 under $H = 100$ Oe. (b, d, f, h) Magnetic hysteresis loops measured at 5 K and 300 K of Co_3O_4 and $\text{CoFe}_x\text{O}_y\text{-SO}_4$ -100, 200, 400.

The bidentate-bond of SO_4^{2-} on the surface of $\text{CoFe}_x\text{O}_y\text{-SO}_4$ can introduce strongly acidic sites playing a role in the OER.²¹ The presence of these acidic sites on $\text{CoFe}_x\text{O}_y\text{-SO}_4$ was evaluated using NH_3 -TPD measurements, using the sulfate-free Co_3O_4 as a reference. As displayed in Figure 4b, Co_3O_4 shows weak NH_3 -desorption peaks, which indicate a moderate density of intrinsic acidic sites on the Co_3O_4 surface. On the other hand, $\text{CoFe}_x\text{O}_y\text{-SO}_4$ shows strong NH_3 -TPD peaks in the same temperature range, which indicates a high density of acidic sites associated with the presence of SO_4^{2-} on the CoFe_xO_y surface.

The EPR spectrum of the catalyst was measured to explore species with unpaired electrons, and particularly oxygen vacancies that could generate high-energy dangling bonds at the catalyst surface (Figure 3.18c).^{42, 43} Using Co_3O_4 as a reference, we observed the signal at $g = 2.12$, associated with the presence of oxygen vacancies V_o , to be strongly enhanced in $\text{CoFe}_x\text{O}_y\text{-SO}_4$. This result demonstrates that the introduction of Fe and sulfate ions generate a large density of oxygen vacancies.

XPS was used to analyze the surface electronic states of the catalyst and to further confirm the presence of sulfate ions on the surface of CoFe_xO_y (Figure 3.18). As shown in Figure 3.26, a clear sulfur signal was detected from all catalysts produced from Mohr's salt. The S 2p spectrum of the $\text{CoFe}_x\text{O}_y\text{-SO}_4$ catalyst exhibits a broad peak that can be fitted with two doublets with S 2p_{3/2} binding energies (BEs) at 168.8 eV and 171.3 eV (S 2p_{3/2}). We observe the higher energy component, which BE coincides with that of sulfur within a sulfate chemical environment, to increase with the amount of Fe and thus SO_4^{2-} introduced.^{20, 44}

The O 1s spectra of $\text{CoFe}_x\text{O}_y\text{-SO}_4$ and Co_3O_4 (Figure 3.18) display 3 to 4 components. The component at lower BE is assigned to lattice oxygen, O_{Lat} . This component is located at 529 eV for Co_3O_4 and shifts to higher BEs with the incorporation of iron. The relative amount of this component detected at the material surface decreases with the amount of iron sulfate introduced. The component at an intermediate BE, at ca. 530-531 eV, is associated with oxygen adsorbed species with a lower oxygen coordination, O_{Ads} .^{45, 46} A second component in the intermediate BE region, at ca. 532 eV, is associated to oxygen

within sulfate ions O_{SO_4} . This component significantly increases with the introduction of larger amounts of ammonium iron sulfate.²² Finally, the component at higher BE, ca. 533–534 eV, is assigned to hydroxyl species and surface adsorbed water, OH_2O . This component also increases and shifts to higher BE with the introduction of Fe and sulfate. The Co 2p XPS spectra from all tested samples display two chemical states, Co^{2+} and Co^{3+} , resembling that of Co within a Co_3O_4 lattice (Figure 3.18e).^{47, 48} With the introduction of Fe and SO_4^{2-} , the peaks broaden and shift to higher BE, which indicates the existence of electronic coupling and electron transfer between cobalt, iron and potentially SO_4^{2-} groups.^{21, 22} Besides, the intensity of the Co XPS signal decreases with the introduction of Fe, consistently with the metal ion exchange and the results obtained from EDX analysis. Figure 3.18f displays the Fe 2p_{3/2} XPS spectra. All spectra can be fitted with two components associated with Fe^{2+} and Fe^{3+} ions within an oxide lattice, although the component at higher BE, could be also assigned to Fe within a FeSO_4 chemical environment.^{23, 31, 49}

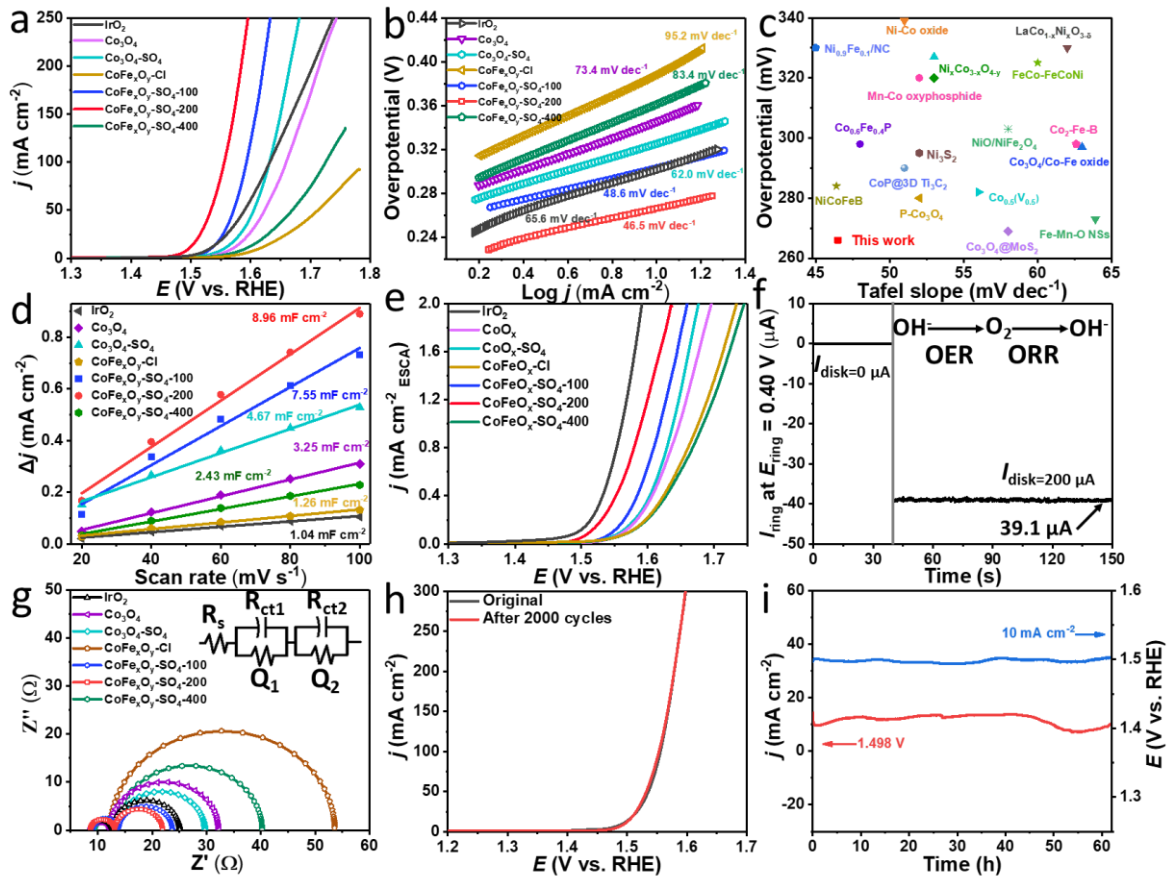


Figure 3.20. Electrocatalytic OER performance of the various catalysts. a) LSV curves. b) Tafel plots. c) Comparison of overpotential at 10 mA cm^{-2} and Tafel slopes for $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$ and

previously reported cobalt-based OER catalysts (Table S5). d) Capacitive current density measured at 1.17 V vs. RHE plotted as a function of scan rate. e) ECSA-normalized OER polarization curves. f) Ring current of CoFe_xO_y-SO₄-200 on an RRDE (1500 rpm) in 1 M KOH solution (ring potential was set at 0.40 V vs. RHE). g) Nyquist plots at the potential of 1.52 V vs. RHE. h) LSV curves of CoFe_xO_y-SO₄-200 before and after 2000 cycles. i) Chronoamperometry at 1.50 V vs. RHE and chronopotentiometry at 10 mA cm⁻² curve of CoFe_xO_y-SO₄-200.

Table S2. Comparison of OER activity of obtained catalyst.

Catalyst	η_{10} [mV]	Tafel Slope [mV dec ⁻¹]
IrO ₂	301	65.6
Co ₃ O ₄	339	73.4
Co ₃ O ₄ -SO ₄	325	62.0
CoFe _x O _y -Cl	383	95.2
CoFe _x O _y -SO ₄ -100	303	48.6
CoFe _x O _y -SO ₄ -200	266	46.5
CoFe _x O _y -SO ₄ -400	361	83.4

Table S3. C_{dl} and ECSAs of various catalysts.

Catalyst	C _{dl} (mF cm ⁻²)	ECSA (cm ⁻²) ^a
IrO ₂	1.04	26.00
Co ₃ O ₄	3.25	81.25
Co ₃ O ₄ -SO ₄	4.67	116.75
CoFe _x O _y -Cl	1.26	31.50
CoFe _x O _y -SO ₄ -100	7.55	188.75
CoFe _x O _y -SO ₄ -200	8.96	224.00
CoFe _x O _y -SO ₄ -400	2.43	60.75
CoFe _x O _y -SO ₄ -200-450°C	5.79	144.75
CoFe _x O _y -SO ₄ -200-550°C	4.65	116.25

Table S4. Simulated parameters from the relevant equivalent circuits

Catalyst	R _s (Ω)	R _{ct1} (Ω)	Q ₁ (S·s ⁿ)	R _{ct2} (Ω)	Q ₂ (S·s ⁿ)
IrO ₂	8.66	12.38	3.28·10 ⁻³	4.04	4.99·10 ⁻⁶
Co ₃ O ₄	8.71	3.52	5.72·10 ⁻⁶	20.04	3.46·10 ⁻³
Co ₃ O ₄ -SO ₄	9.03	4.59	1.71·10 ⁻³	16.07	7.25·10 ⁻⁶
CoFe _x O _y -Cl	8.90	3.40	5.08·10 ⁻⁶	41.29	3.90·10 ⁻³
CoFe _x O _y -SO ₄ -100	9.06	4.76	6.03·10 ⁻⁶	9.89	1.56·10 ⁻³
CoFe _x O _y -SO ₄ -200	8.62	4.50	4.90·10 ⁻⁶	8.78	2.90·10 ⁻⁷

CoFe_xO_y-SO₄-400	9.35	4.05	$2.07 \cdot 10^{-3}$	26.85	$2.83 \cdot 10^{-5}$
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The OER activities of the different catalysts were initially assessed using linear sweep voltammetry (LSV) with a conventional three-electrode set-up in a 1 M KOH electrolyte. A commercial IrO₂ electrocatalyst was also tested as a reference. As shown in Figure 3.20a, Co₃O₄ exhibits a large overpotential of 339 mV at a current density of 10 mA cm⁻², indicating a poor OER activity. After sulfate modification, the overpotential of Co₃O₄-SO₄ decreased to 325 mV at 10 mA cm⁻². By additionally incorporating iron, OER activity was strongly improved with an overpotential down to 266 mV at 10 mA cm⁻² for CoFe_xO_y-SO₄-200, well below that of the IrO₂ electrode (301 mV). This result demonstrates Fe to play an important role in the OER. However, when large amounts Fe were introduced, a negative effect on the OER performance was observed, as shown for the CoFe_xO_y-SO₄-400 sample that was characterized by a large overpotential (361 mV). This result demonstrates that Co also plays an important role in the OER, and thus an optimum Co/Fe ratio exists. Besides, the sulfate-free sample containing Co and Fe, CoFe_xO_y-Cl, also displayed a very poor OER performance, demonstrating the important role played by sulfate ions. In addition, an increase in the annealing temperature also resulted in a strong decrease in catalytic activity, which is related to the collapse of the porous structure and the crystallization of the material (Figure S18).

As shown in Figure 3.20b, CoFe_xO_y-SO₄-200 exhibited the best reaction kinetics with the smallest Tafel slope (46.5 mV dec⁻¹) among all catalysts tested, including the commercial IrO₂. Moreover, CoFe_xO_y-SO₄-200 also exhibits superior OER activity and kinetics than most previously reported oxide OER electrocatalysts (Figure 3.20d, Table S5).

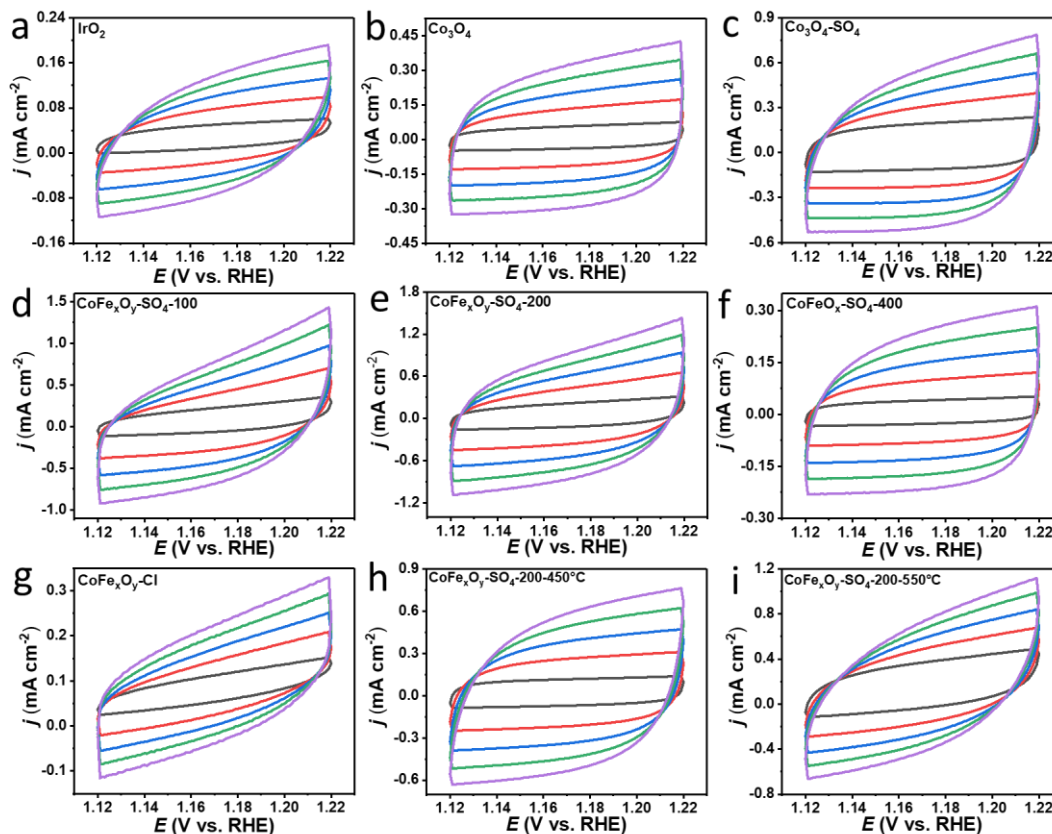


Figure 3.21. Cyclic voltammograms of a) IrO_2 ; b) Co_3O_4 ; c) $\text{Co}_3\text{O}_4\text{-SO}_4$; d) $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-100}$; e) $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$; f) $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-400}$; g) $\text{CoFe}_x\text{O}_y\text{-Cl}$; h) $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200-450}^\circ\text{C}$ and f) $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200-550}^\circ\text{C}$ in the non-faradaic region of 1.12-1.22 V vs. RHE at various scan rates.

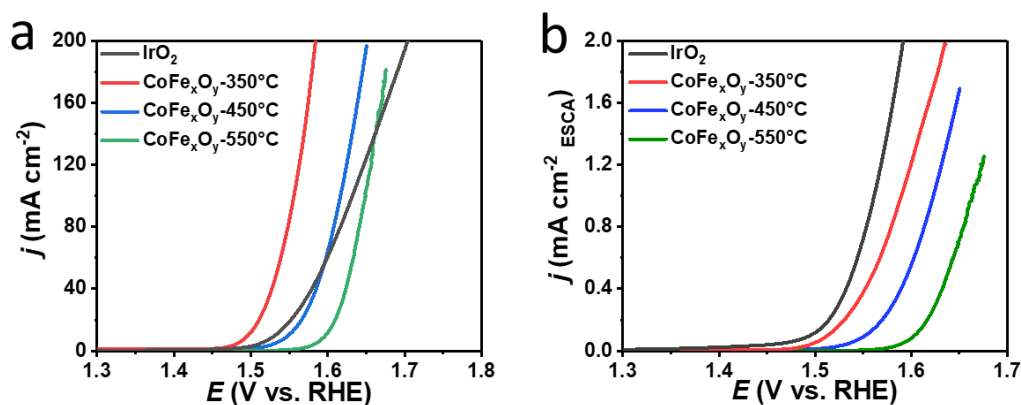


Figure 3.22. OER polarization curves for (a) different annealing temperature $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$ and IrO_2 , (b) ECSA-normalized) different annealing temperature $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$ and IrO_2 in 1.0 M KOH.

The ECSA was estimated from the double-layer capacitance (C_{dl}) measured by cyclic voltammetry (CV) at different scanning rates (Figure 3.21).^{24, 50} C_{dl} was calculated from the slope of the linear fitting for the charge current versus the scan rate (Figure 3.20d, Table S3). Using a specific capacity of 0.04 mF cm^{-2} , ECSA was estimated at 224 cm^2 for $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$, well above that of the other catalysts evaluated (Table S3). Figure 5e displays the specific activity obtained by normalizing the current to the ECSA. Despite its much larger ECSA, $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$ also displayed the highest specific activity.⁵¹ This high activity is related to a combination of different parameters, including a proper Co/Fe ratio, the presence of sulfate ions, the amorphous structure of the material and its highly porous nanosheet-based geometry.

A rotating ring-disk electrode (RRDE) was used to characterize the Faradaic efficiency (FE) of the best performing catalyst, $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$. As shown in Figure 3.20f, the disk current was held constant at $200 \text{ }\mu\text{A}$ while the ring potential was set at 0.40 V vs. RHE, rendering a continuous OER (disk electrode) $\rightarrow$ ORR (ring electrode) process. That is, O_2 molecules generated from the $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$ catalyst surface on the disk electrode were rapidly reduced on the Pt ring electrode under ORR potential.⁵² In these conditions, a ring current of $39.1 \text{ }\mu\text{A}$, with a collection efficiency of 0.2 , was determined. Thus the calculated FE was 97.8% , which confirms that the measured oxidation current on $\text{CoFe}_x\text{O}_y\text{-SO}_4$ provides from the OER.

Figure 3.20g displays the Nyquist plots of the EIS data obtained from the different electrocatalysts. The measured semi-circles result from the rough surface structure of the electrodes and were accounted for using a constant phase element (Q) introduced to simulate a double-layer capacitor (C_{dl}). Because the OER involves at least two electrochemical processes, the formation of intermediates and subsequently O_2 , an equivalent circuit with two charge-transfer processes was considered to fit the EIS plots. Q_1R_{ct1} represents the formation of the active intermediates and Q_2R_{ct2} the oxygen evolution process. Besides, R_s accounts mainly for the resistance of the electrolyte between the working and reference electrodes.^{53, 54} Table S4 lists the parameters used for the EIS fitting. The smallest R_{ct} values obtained for $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$ indicate the faster charge-transfer process taking place in this catalyst.

Figure 3.20h shows the LSV curves of the $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$ after successive CV tests. The overpotential needed to catalyze water oxidation at 10 mA cm^{-2} was virtually the

same before and after 2000 cycles test. Moreover, the chronoamperometry (i-t) and chronopotentiometry (E-t) durability test for $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$ at the overpotential of 266 mV and 10 mA cm^{-2} , respectively, showed no obvious activity decay during 60 h of continuous test (Figure 3.20i), indicating that the $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$ catalysts have excellent stability under the electrochemical conditions of water oxidation.

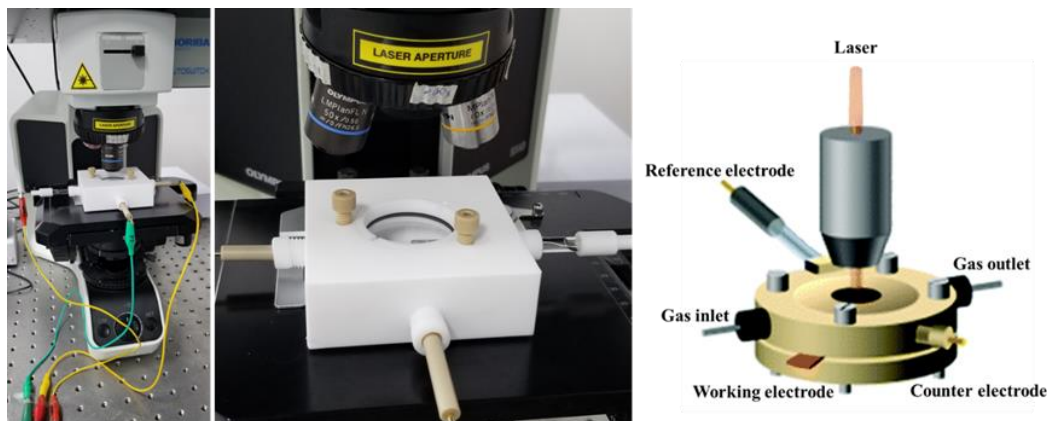


Figure 3.23. Picture and schemes of the in-situ Raman spectrometry set-up.

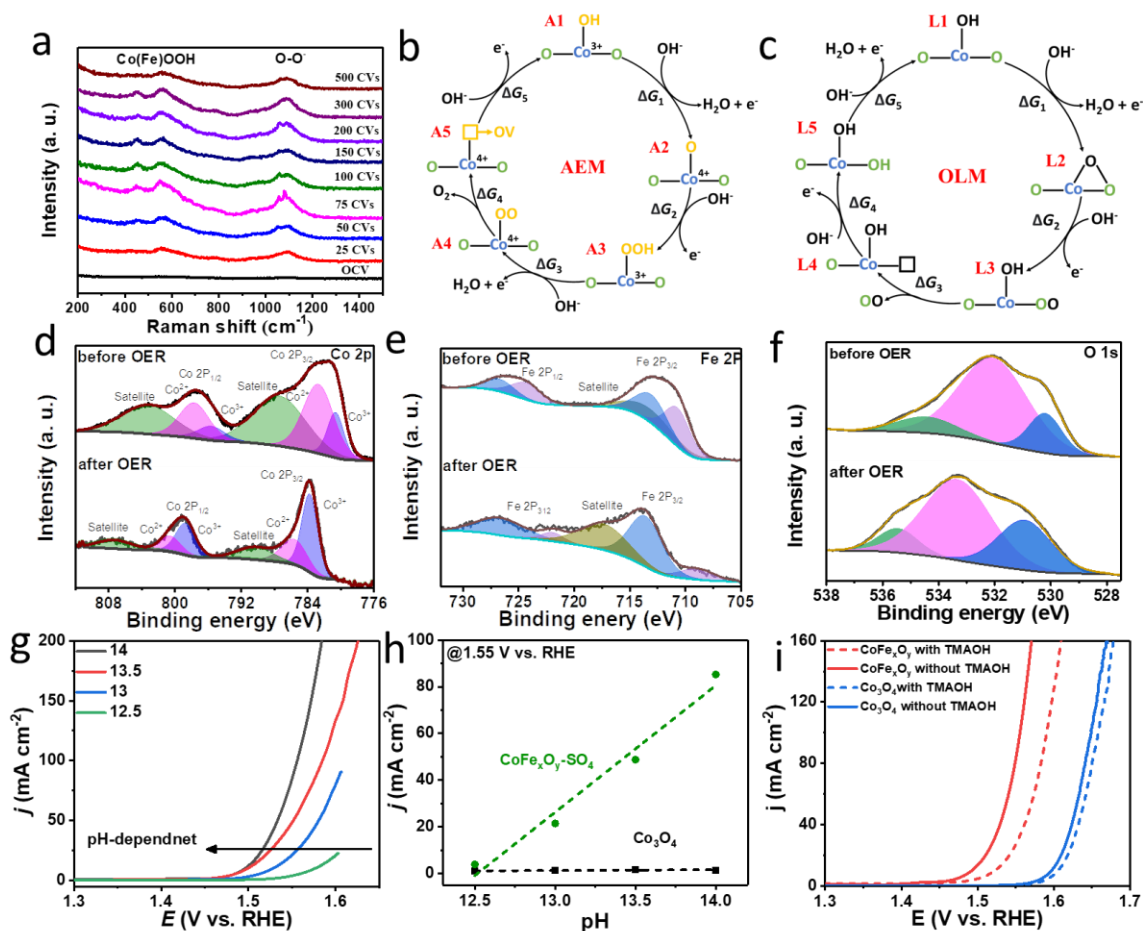


Figure 3.24. a) In situ Raman spectra of $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$ after several CV cycles in 1.0 M KOH electrolyte. b-c) Scheme of the AEM and LOM OER processes, where $\square$ represents an oxygen vacancy. d-f) High-resolution O 1s, Co 2p and Fe 2p_{3/2} XPS spectra of $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$ before and after OER process. g) OER polarization curves of $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$ at different pH values. h) Current densities $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$ and Co_3O_4 at 1.5 V vs. RHE as a function of the pH value. i) OER polarization of $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$ and Co_3O_4 in 1 M KOH without and with TMAOH, respectively.

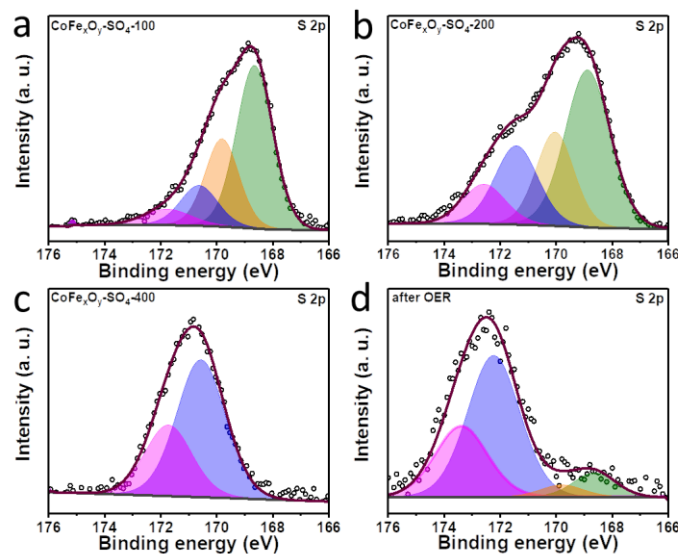


Figure 3.25. S 2p high-resolution XPS spectra of a) $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-100}$, b) $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$, c) $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-400}$ and d) $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$ after long-term OER.

To gain additional insight into the reaction kinetics of $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$ catalyst and its evolution, in-situ Raman spectroscopy analyses were carried out at a potential of 0.60 V vs. Hg/HgO under a 1.0 M KOH electrolyte (Figure 3.23). As shown in Figure 3.24a, after 200 CV cycles and above, the Raman spectra displayed a new broad peak at 550-600 cm^{-1} , corresponding to the A_{1g} and E_g vibrational modes of Co-O in CoOOH .^{48, 54} Increasing the number of cycles, the peak intensity increased, which is correlated with an increase of the oxyhydroxide phase and points towards the conversion of the mixed-metal oxide surface to an oxyhydroxide. Besides, an additional band was observed in the 1000-1200 cm^{-1} range (peaking at ca. 1090 cm^{-1}), which is assigned to a superoxidic species (CoOO^-).⁵⁵ The intensity of this band also increased with cycling, demonstrating the generation and progressive accumulation of this species during the OER process.

XPS analysis of the material after OER shows a shift of the Co 2p XPS spectrum to higher BEs, with its peaks becoming slightly narrower (Figure 3.24d). This result points toward the material oxidation from a mixture of Co^{2+} and Co^{3+} , to Co^{3+} , consistently with the surface conversion to metal oxyhydroxide observed by in situ Raman measurements.⁵² Besides, the rest of the XPS spectra, and particularly the Fe 2p and O 1s regions, also slightly shift to lower BEs after OER test (Figure 6e,f), which points towards the creation of an upward band bending at the material surface associated to a surface charge depletion, or a bulk-related downward shift of the Fermi level related to an increase of the hole concentration.

In most electrocatalysts, OER proceeds through the adsorbate evolution mechanism (AEM, Figure 3.24b). This conventional mechanism requires catalysts with proper adsorption sites, i.e. surface sites that bind reactants, intermediates and products neither too strongly nor too weakly.^[56, 57] Recent works have evidenced that some OER oxide catalysts are particularly active due to the participation of lattice oxygen in the reaction (Figure 3.24c).^[58-61] In this lattice oxygen oxidation mechanism (LOM), the OER involves a direct O-O coupling, which bypasses the highly correlated intermediates adsorption in AEM, thus resulting in higher OER activities.

In a metal oxyhydroxide (MOOH), the LOM involves several steps as simplified in Figure 3.24c.^[15] Briefly, the first steps involve the interaction with hydroxide ions in solution, the deprotonation of OH⁻ groups within the oxyhydroxide, and the release of H₂O. Subsequently, O-O bonds are formed within the oxide structure and O₂ is released. The released O₂ incorporates two types of oxygen, one from adsorbed OH⁻ and the other from the MOOH lattice.^{62, 63} Thus the release of O₂ leaves an oxygen vacancy behind, which is filled through the adsorption of additional OH⁻.⁶⁴ The last step is the adsorption of an additional OH⁻ and the release of an H₂O molecule to return the catalyst to its initial state.

In the LOM, the catalyst performance does not rely on how close to the top of a volcano-like trend their surface adsorption sites lay, but on the strength of the metal-oxygen bonds and the suitability of the catalyst surface but also bulk electronic structure. These parameters can be tuned by adjusting the catalyst composition and structure. The variable valence of some transition metals, such as cobalt and iron, facilitates LOM. Under basic conditions, during OER, transition metal ions are easily oxidized to higher valence states, which act as catalytic active sites. Besides, the amorphous structure of the material not only provides a higher density of undercoordinated atoms that enhance the adsorption of hydroxyl groups, but also facilitates the change of oxidation state and promotes the participation of lattice oxygen in the OER.

In the LOM, the rate-limiting step is the deprotonation of hydroxyl groups. Thus, the LOM-OER kinetics strongly depends on the electrolyte pH.^{65, 66} On the other hand, the AEM-OER activity is limited by four concerted proton-electron transfer steps on surface metal centers, yielding a pH-independent performance. As displayed in Figure 6g, h, in contrast with the results obtained from Co₃O₄, the onset potential of CoFe_xO_y-SO₄

strongly decreases with increasing pH, pointing toward non-concerted proton transfer steps within LOM as the rate-limiting steps in the OER on this sample.

Another fundamental characteristic of LOM is the direct O-O coupling, which bypasses the need for correlated intermediate adsorption in the AEM. Thus, to distinguish LOM from AEM one can track the generation of peroxo-like (O_2^{2-}) and superoxo-like (O_2^-) species. Here we tracked the existence of these negatively charged oxygenated species by introducing tetramethylammonium cations (TMA^+) as a chemical probe into the KOH electrolyte (1 M KOH + 1 M TMAOH).^{52, 61} TMA^+ specifically binds with negative oxygenated species, thus hampering the OER via LOM. As shown in Figure 3.24i, when introducing TMAOH into the KOH solution, the OER activity of $\text{CoFe}_x\text{O}_y\text{-SO}_4$ was significantly reduced, which demonstrates the key contribution played by LOM in this material. On the other hand, Co_3O_4 showed just a minor change of OER performance in the presence of 1 M TMAOH. Overall, these results suggest the high OER activity of OER $\text{CoFe}_x\text{O}_y\text{-SO}_4$ to be associated with the key role played by the LOM.

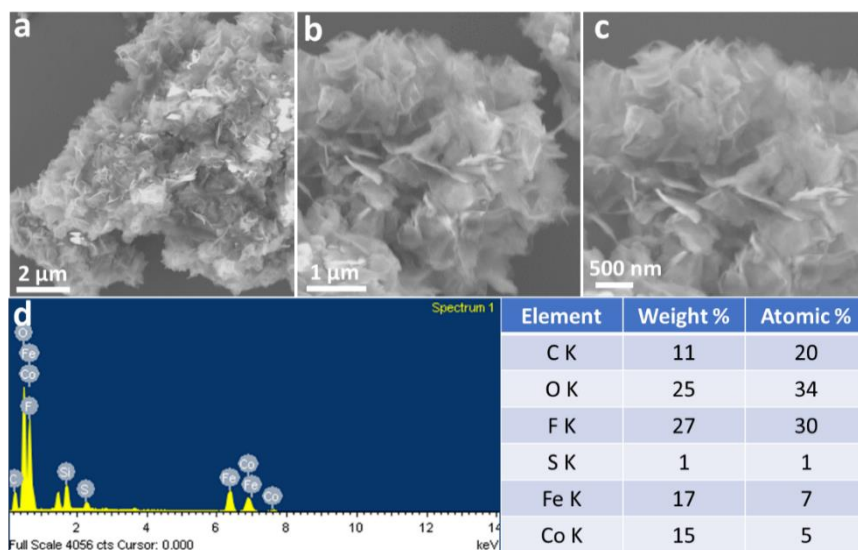


Figure 3.26. (a-c) SEM images and (d) EDX spectrum of $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$ after long-term OER testing.

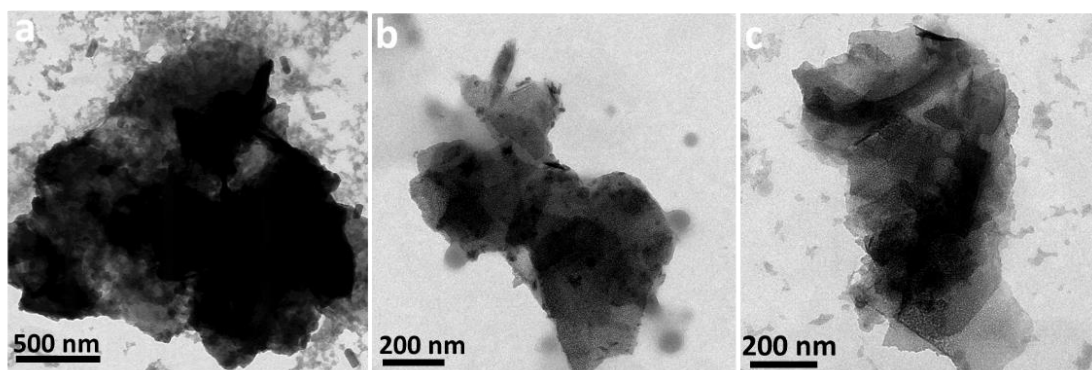


Figure 3.27. TEM images of $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$ after long-term OER testing.

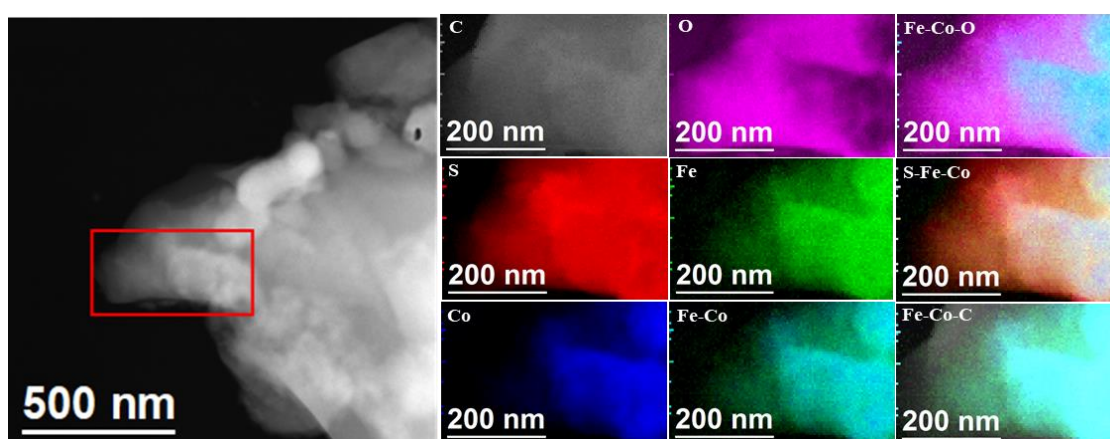


Figure 3.28. EELS chemical composition maps of $\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$ obtained from the red squared area of the STEM micrograph after long-term OER testing. Individual S L2,3-edges at 165 eV (red), Fe L2,3-edges at 708 eV (green), Co L2,3-edges at 779 eV (blue), O K-edge at 532 eV (pink) and C K-edge at 284 eV (grey) and composites of Fe-Co, Fe-Co-O and S-Fe-Co and Fe-Co-C.

After a long-term OER process, the catalyst was collected and analyzed. As shown in SEM and TEM images in Figures 3.26 and 3.27, the post-OER product maintained the ultrathin nanosheet structure with no obvious change. Moreover, both EDS elemental maps and HAADF-STEM images demonstrate the homogenous distribution of O, S, Co and Fe to be preserved in the reacted material. (Figure 3.28).

Table S5. OER activity of $\text{CoFe}_x\text{O}_y\text{-SO}_4$ and other Co-based catalysts in 1M KOH electrolyte.

Catalyst	η_{10}	Tafel Slope	References
	[mV]	[mV dec ⁻¹]	
$\text{CoFe}_x\text{O}_y\text{-SO}_4\text{-200}$	266	46	This work

A-FeCoSeO _x -100	294	45	67
Co ₃ O ₄ /Co-Fe oxide	297	63	68
FeCo oxyhydroxides	277	110	69
Fe-doped Co ₃ O ₄	380	60	70
Co ₃ O ₄ /NiCo ₂ O ₄	340	88	71
Co ₃ O ₄ nanotubes	390	76	72
NiCoFeB	284	46	73
Co ₂ -Fe-B	298	63	74
FeCo-FeCoNi	325	60	75
Ni _x Co _{3-x} O _{4-y}	320	53	76
Co _{0.6} Fe _{0.4} P	298	48	77
Ni _{0.6} Co _{1.4} (OH) ₂	300	80	78
N-CoFe LDHs	281	40	79
LaCo _{1-x} Ni _x O _{3-δ}	330	62	80
Co _{0.5} (V _{0.5})	282	56	81
P-Co ₃ O ₄	280	52	82
Co ₃ O ₄ @MoS ₂	269	58	83
Ni-Co oxide	340	51	84
Co _x Fe _{1-x} WO ₄	327	53	85
NiO/NiFe ₂ O ₄	303	58	86
Mn-Co oxyphosphide	320	52	87

1. Conclusion

In summary, cobalt-iron oxide nanosheet containing SO_4^{2-} anionic groups were produced from the etching and partial cation exchange of a cobalt-based ZIF-67 with an ammonium iron sulfate. We show how this salt breaks the polyhedral structure of ZIF-67, yielding porous assemblies of nanosheets, containing controlled amounts of iron and sulfate ions. The material composition and crystal structure can be adjusted to optimize its OER performance. The optimized $\text{CoFe}_x\text{O}_y\text{-SO}_4$ sample displays an OER overpotential of 268 mV at 10 mA cm^{-2} , a Tafel slope of 46.5 mV dec^{-1} , and excellent stability during 62 h. We demonstrated this excellent performance to be associated with the presence of the three elements, cobalt, iron and sulfate ions, and to the porous and amorphous structure of the material. Raman spectroscopy analysis correlated with XPS data probes the material to be further oxidized to an oxohydroxide phase. It is further demonstrated here, that $\text{CoFe}_x\text{O}_y\text{-SO}_4$ samples catalyse the OER through an effective LOM mechanism.

3.5 Conclusions

In summary, cobalt-Iron oxide nanosheet containing SO_4^{2-} anionic groups were produced from the etching and partial cation exchange of a cobalt-based ZIF-67 with an ammonium iron sulfate. We show how this salt breaks the polyhedral structure of ZIF-67, yielding porous assemblies of nanosheets, containing controlled amounts of iron and sulfate ions. The material composition and crystal structure can be adjusted to optimize its OER performance. The optimized $\text{CoFe}_x\text{O}_y\text{-SO}_4$ sample displays an OER overpotential of 268 mV at 10 mA cm^{-2} , a Tafel slope of 46.5 mV dec^{-1} , and excellent stability during 62 h. We demonstrated this excellent performance to be associated with the presence of the three elements, cobalt, iron and sulfate ions, and to the porous and amorphous structure of the material. Raman spectroscopy analysis correlated with XPS data probes the material to be further oxidized to an oxohydroxide phase. It is further demonstrated here, that $\text{CoFe}_x\text{O}_y\text{-SO}_4$ samples catalyse the OER through an effective LOM mechanism.

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Chapter 4

MOF-derived ultrathin cobalt molybdenum phosphide nanosheets for efficient electrochemical overall water splitting

4.1 Abstract

The development of high-performance and cost-effective earth-abundant transition metal-based electrocatalysts is of major interest for several key energy technologies, including water splitting. Herein, we report the synthesis of ultrathin CoMoP nanosheets through a simple ion etching and phosphorization method. The obtained catalyst exhibits outstanding electrocatalytic activity and stability towards oxygen and hydrogen evolution reactions (OER and HER), with overpotentials down to 273 and 89 mV at 10 mA cm^{-2} , respectively. The produced CoMoP nanosheets are also characterized by very small Tafel slopes, 54.9 and 69.7 mV dec^{-1} for OER and HER, respectively. When used as both cathode and anode electrocatalyst in the overall water splitting reaction, CoMoP-based cells require just 1.56 V to reach 10 mA cm^{-2} in alkaline media. This outstanding performance is attributed to the proper composition, weak crystallinity and two-dimensional nanosheet structure of the electrocatalyst.

4.2 Introduction

Hydrogen, with a high gravimetric energy density (142 MJ kg^{-1}) and zero-carbon emissions, is both a key component in the chemical industry and a very appealing energy carrier for clean and sustainable energy storage and supply.^{1, 2} Since molecular hydrogen is not freely available in nature, it needs to be extracted from hydrogen-containing compounds. Currently, fossil fuels are the main source of H_2 , which involves the release of large amounts of carbon. The electrochemical water splitting is the main green alternative to produce H_2 , but it is seriously hampered by the high cost and insufficient durability of current electrocatalysts, based on scarce noble metals such as Pt, Ir and Ru,³⁻⁶ and the slow kinetics of the hydrogen and oxygen evolution reactions (HER, OER),

which makes water electrolysis not competitive with steam reforming of natural gas or coal gasification processes.⁷⁻⁹

To overcome the current challenges and enable the massive production of H₂ by water splitting, substantial efforts have been devoted to the development of high activity, stable and cost-effective electrocatalysts for overall water splitting (OWS). Among the wide range of materials proposed for alkaline water electrolysis, including metal oxides/hydroxides,¹⁰⁻¹² chalcogenides,¹³⁻¹⁶ nitrides^{17, 18} and carbides^{19, 20}, metal phosphides have demonstrated particularly attractive catalytic performances.^{21, 22} The outstanding performance of phosphides has been related to their high electrical conductivity, favorable electronic structure, and high stability against corrosion.^{23, 24} Amongst phosphides, cobalt phosphide (CoP) exhibits an exceptional HER activity associated with a proper electronic structure and specifically to the effective capture of protons by the negatively charged phosphorous atoms.^{25,26} Besides, CoP is also characterized by a very high OER activity associated with the high ability of the positively charged cobalt cations to adsorb oxygen intermediates while the negatively-charged P facilitate the desorption of O₂ molecules.^{27,28} However, the OWS in CoP still requires too large overpotentials for practical applications, mainly ascribed to the high dissociation energy of water and the sluggish OER kinetics involving a multi-electron transfer process.^{29, 30}

An effective strategy to optimize a material's performance is the introduction of an additional element that provides additional degrees of freedom to modulate its electronic structure and surface properties. Within transition metal phosphide electrocatalysts, additional metals enable a fine-tuning of the d-band position, optimizing the adsorption free energy of the reactants/intermediates/products, and thus improving the catalytic activity and even stability. In this direction, Xiao et al. reported the HER catalytic activity of CoP to be boosted by vanadium doping.³¹ The introduced V strongly interacts with the hosted Co atoms, enhancing the VCoP electron density and thus accelerating the HER. Other elements, such as Zn,³² Mn,³³ Ni,³⁴ Ce,³⁵ Cr,³⁶ and W,²¹ have been also demonstrated to promote either the HER or OER through enhancing electron interactions.²⁸

Beyond composition, the structure, morphology and organization of the catalyst particles are key parameters defining the density, accessibility and activity of the catalytic sites, which ultimately determine the catalytic activity. In this regard, metal-organic

frameworks (MOFs), with a crystalline and porous structure formed by metal ion/cluster bridged by organic ligands, have been demonstrated as excellent sacrificial templates to produce porous carbon-based nanomaterials with tuned composition and morphology.³⁷⁻

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Inspired by the above considerations, we have rationally designed a novel and highly effective bifunctional electrocatalyst for OWS. This new catalyst is based on CoP, structured as 2D ultrathin nanosheets and derived from the ZIF-67 MOF. It includes Mo^{6+} as a high valence 4d transition metal ion, which ionic radius of 0.62 Å matches well with that of Co^{3+} (0.63 Å), thus allowing the substitution of Co^{3+} by Mo^{6+} within the CoP lattice.^{41, 42} We demonstrate here, that the proposed porous nanosheet-based structure and the in-corporation of Mo within the CoP lattice enables a rapid water dissociation and effective and stable HER and OER performances.

4.3 Experimental Section

4.3.1 Chemicals

Ammonium molybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, 90%), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, 99.9%), potassium hydroxide (KOH, 85%), iridium(IV) oxide (IrO_2 , 99.9% metal basis), and Nafion (5 wt% in a mixture of low aliphatic alcohols and water) were obtained from Sigma-Aldrich. 2-Methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$, 99%) was purchased from Acros Organics. Methanol, ethanol and isopropanol were of analytical grade and obtained from various sources. Milli-Q water was obtained from a Purelab flex from Elga. All chemicals were used as received, without further purification.

4.3.2 Preparation of ZIF-67

ZIF-67 was produced following a previously reported procedure with some modifications.^{16, 43} Briefly, 0.87 g $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ was dissolved in 30 mL of methanol to obtain a clear solution. Subsequently, the above solution was poured into 30 mL of methanol containing 1.97 g of 2-methylimidazole under vigorous stirring. After mixing completely, the solution was incubated for 24 h at room temperature. Purple precipitates were collected by centrifugation, washed with methanol at least three times, and finally dried at 60 °C overnight.

4.3.3 Preparation of Mo-Co MOFs

120 mg of as-prepared ZIF-67 powder was ultrasonically re-dispersed in 20 mL of ethanol. This solution was poured into 100 mL of an aqueous solution containing 50 mg, 100 mg, 200 mg ammonium molybdate under continuous magnetic stirring. The mixture was then stirred vigorously for 24 hours at room temperature. Lavender precipitates were collected by centrifugation, washed with water at least three times, and finally freeze-dried overnight.

4.3.4 Preparation of CoP and CoMoP

The obtained ZIF-67 and Mo-Co MOFs powders were placed in a porcelain boat within a horizontal tube furnace. In another boat, a 20x mass amount of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ was placed at the upstream side of the tube furnace. The material was then annealed at 350 °C under N_2 flow. After calcination for 2 h, the final black products were denoted as CoP and CoMoP, respectively.

4.3.5 Structural characterization

Powder X-ray diffraction (XRD) was performed on a Bruker AXS D8 Advance X-ray diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Scanning electron microscopy (SEM) analysis was conducted with a Zeiss Auriga microscope equipped with an energy dispersive spectroscopy (EDS) detector operating at 20 kV. Transmission electron microscopy (TEM), High-resolution TEM (HRTEM), Annular dark-field scanning transmission electron microscope (HAADF-STEM) and electron energy loss spectroscopy (EELS) analysis were obtained using a field emission gun FEI Tecnai F20 microscope with a Gatan Quantum filter at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a SPECS system equipped with an Al anode XR50 source operating at 150 W and a Phoibos 150 MCD-9 detector.

4.3.6 Electrochemical Measurements

The electrochemical measurements were carried out by using an electrochemical workstation (CHI 760E, CH Instruments) in a standard three-electrode system in 1 M KOH solution (PH = 14). A graphite rod was used as the counter electrode and a Hg/HgO was employed as the reference electrode. Electrochemical impedance spectroscopy (EIS) was measured within a frequency from 0.01 Hz to 10 kHz at 10 mV amplitude. The

electro-chemically active surface areas (ECSAs) were estimated from the electrochemical double-layer capacitance (C_{dl}) via cyclic voltammetry measurements in a non-faradaic region at various scan rates ($v = 20, 40, 60, 80$ and $100 \text{ mV}\cdot\text{s}^{-1}$). The accelerated stability was assessed by CV for 3000 cycles at a scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$ and the long-term stability tests were performed by chronopotentiometry at about $10 \text{ mA}\cdot\text{cm}^{-2}$. The OWS test was implemented in a two-electrode system with the voltage range of $0\text{--}2.0 \text{ V}$ at a scan rate of 5 mV s^{-1} in 1.0 M KOH electrolyte.

4.4 Results and Discussion

4.4.1 Characterization of electrocatalysts

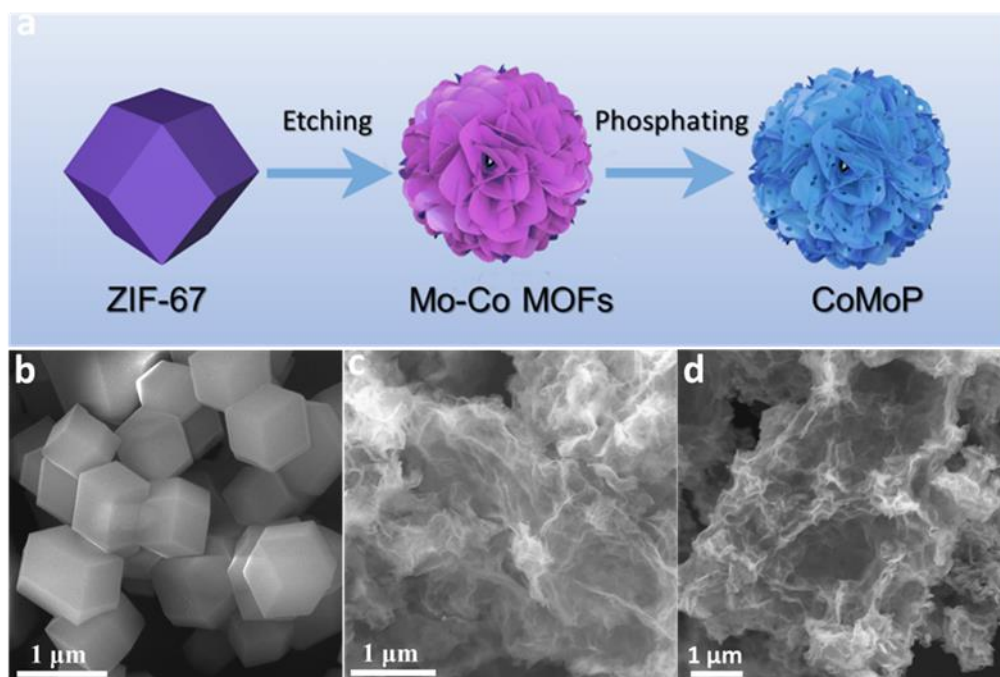


Figure 4.1. (a) Schematic illustration of the CoMoP synthesis process. (b-d) SEM image of (b) ZIF-67 (c) Mo-Co MOFs and (d) CoMoP.

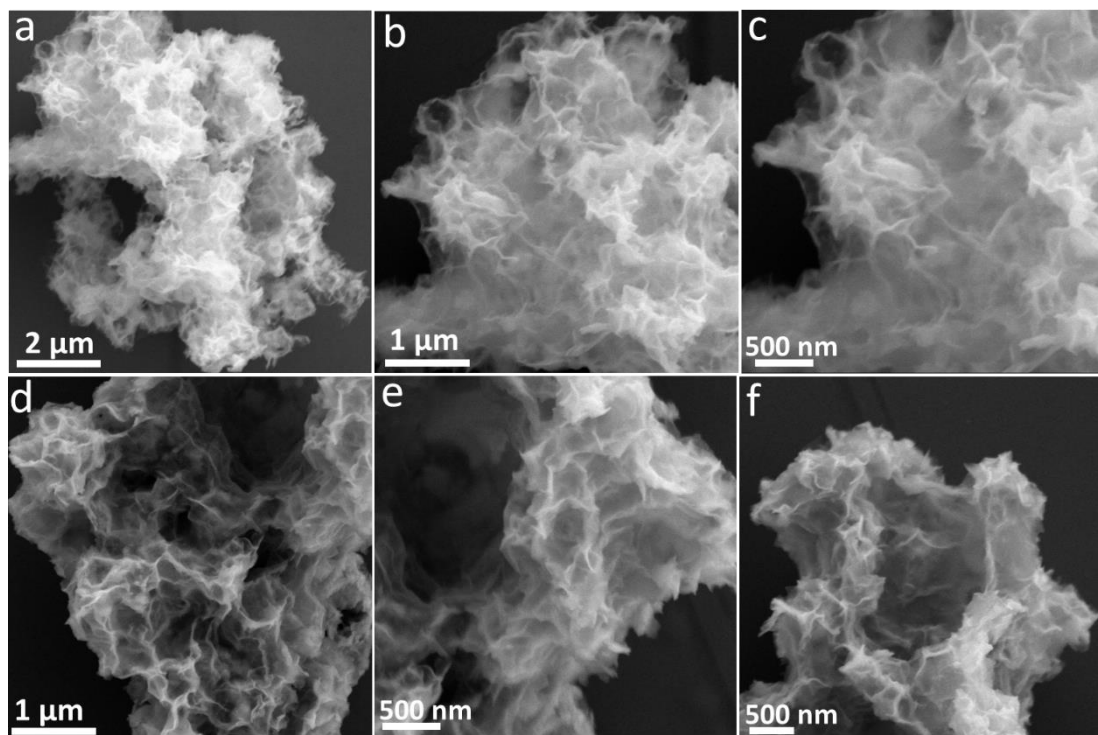


Figure 4.2. SEM images of CoMoP.

CoMoP nanosheets were produced by a three-step process involving the synthesis of a Co-MOF, its etching and partial cation exchange, and a final phosphorization step, as schematically illustrated in Figure 4.1a. First, a cobalt-based zeolitic imidazolate framework (ZIF-67), consisting of polyhedral-shaped micrometer size particles, was produced as a self-sacrificial template (Figure 4.1b). The ZIF-67 was reacted with ammonium molybdate with the double role of etching the structure and partially replacing Co^{3+} cations by Mo^{6+} , yielding a porous wrinkled nanosheet-based material that we refer to as Co-Mo MOF (Figure 4.1c). Finally, the Co-Mo MOF was annealed within a tube furnace containing NaH_2PO_2 at 350 °C for 2 h to produce a porous phosphide with a similar wrinkled nanosheet-based morphology, that we denote as CoMoP (Figures 4.1d and 4.2). EDS analysis of CoMoP showed a Co-Mo atomic ratio of $\text{Co}/\text{Mo} = 4$, and a phosphorus-metal atomic ratio of $\text{P}/\text{M} = 2.6$ ($\text{M} = \text{Co} + \text{Mo}$) (Figure 4.2).

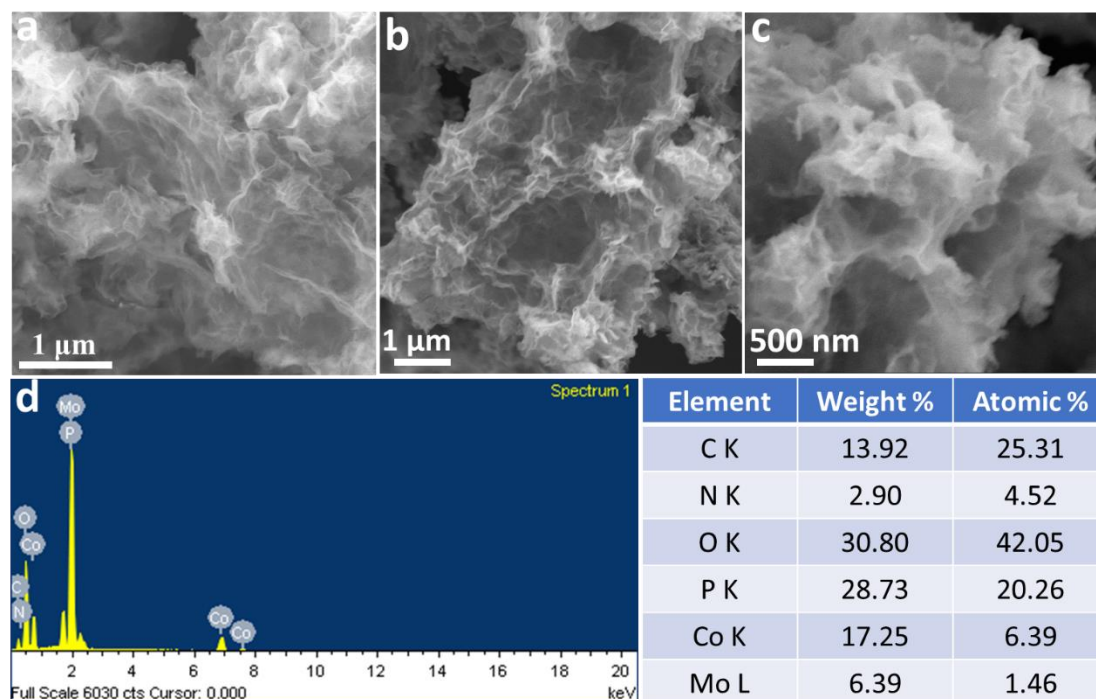


Figure 4.3. a) SEM image of Co-Mo MOFs. b-c) SEM images and d) EDX spectrum of CoMoP.

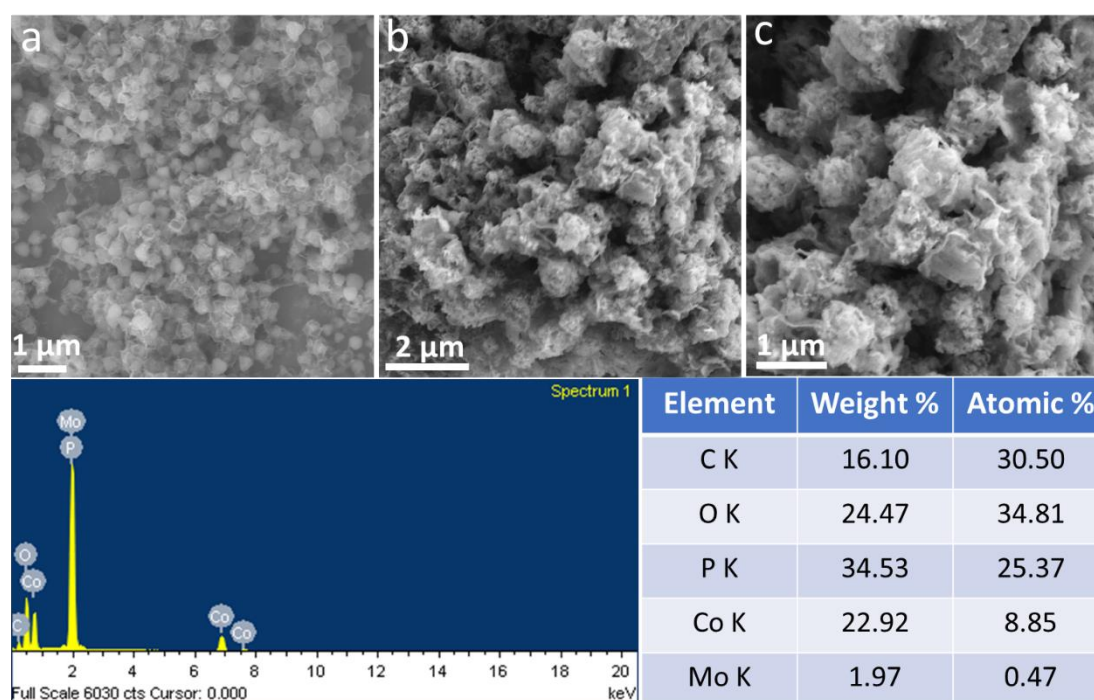


Figure 4.4. a) SEM image of $\text{Na}_2\text{MoO}_4\text{-ZIF-67}$. b-c) SEM images and d) EDX spectrum Mo-CoP.

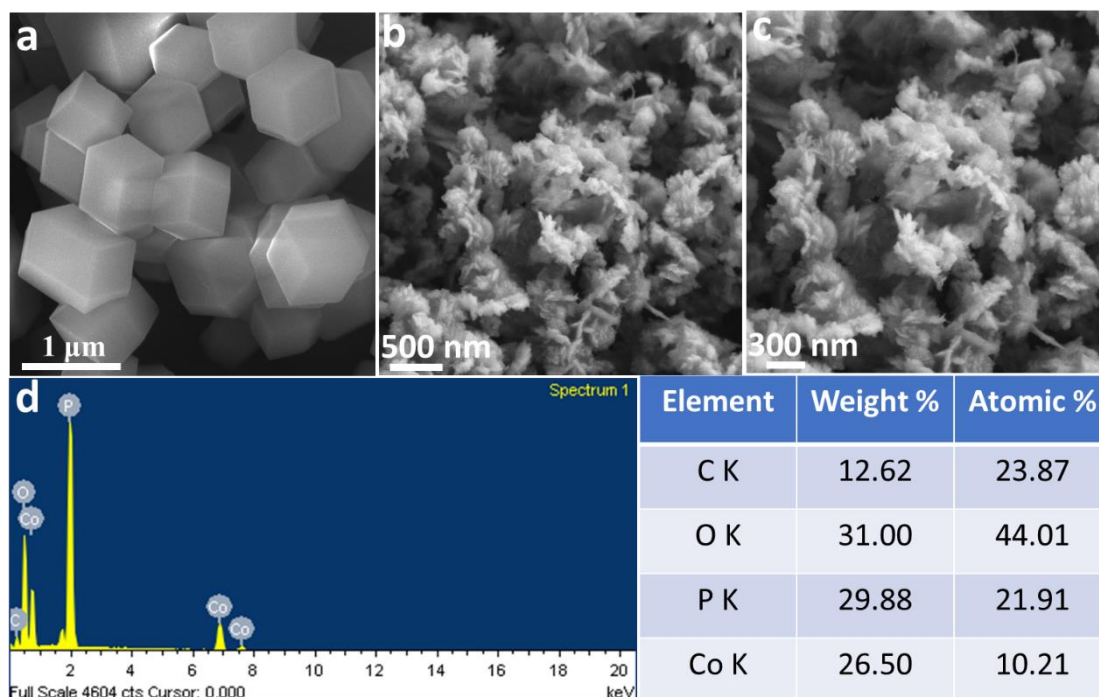


Figure 4.5. a) SEM image of ZIF-67. b-c) SEM images and d) EDX spectrum CoP.

To study the effect of ammonium molybdate, we replaced this chemical with an alternative Mo precursor. Using sodium molybdate as Mo source, the morphology of the final product was much more compact, consisting of partially porous cubes (Figure 4.4). Besides, EDS analysis revealed the molybdenum content of this material to be much lower ($\text{Co/Mo}=18.8$) than that of CoMoP. We will refer to this material as Mo-CoP. As a reference, a Mo-free CoP was obtained by directly annealing the ZIF-67 in the presence of the phosphorous source, with no etching step (Figure 4.5). The obtained material also displayed a more compact geometry than that of the CoMoP nanosheets.

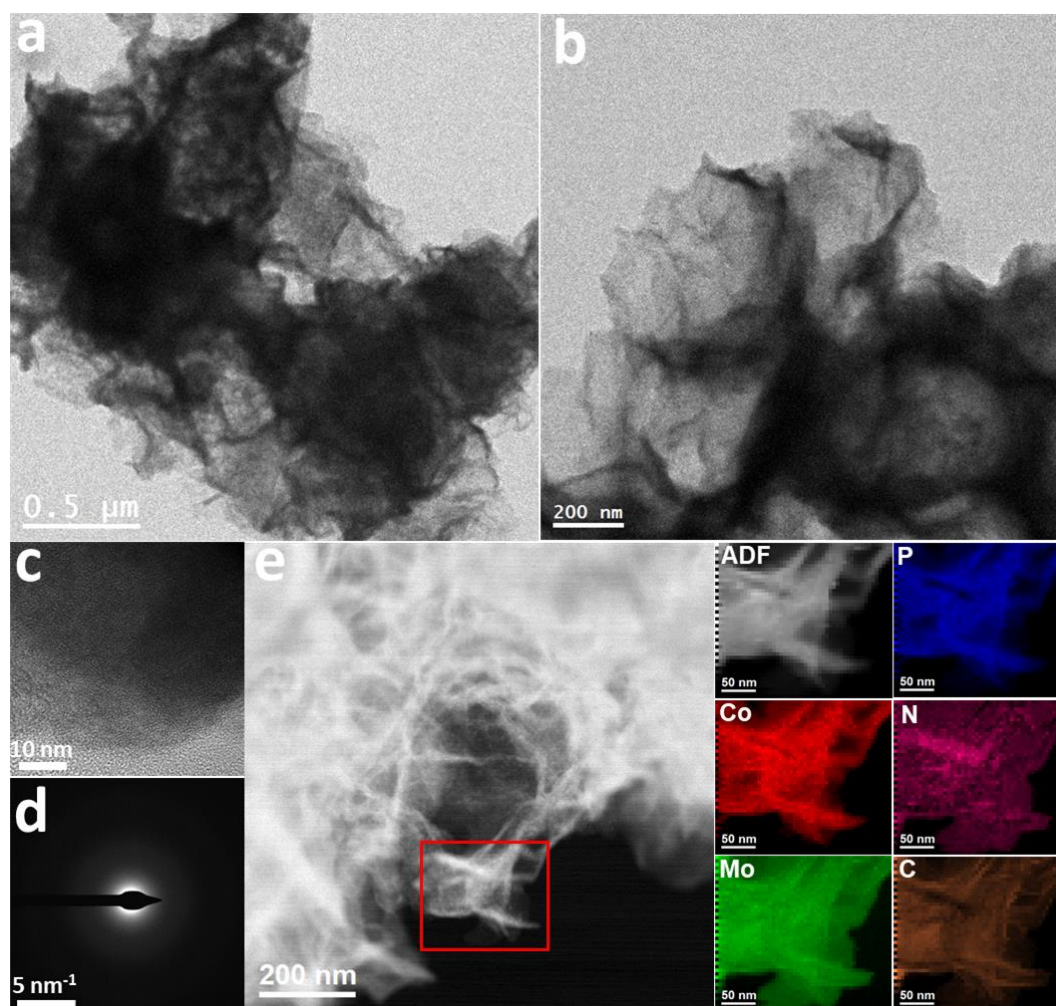


Figure 4.6. (a-b) TEM images, (c) HRTEM image, (d) SAED pattern and (e) HAADF STEM image and EELS chemical composition maps obtained from the red squared area of the STEM micrograph. Individual Co $L_{2,3}$ -edges at 779 eV (red), Mo $M_{4,5}$ -edges at 230 eV (green), P $L_{2,3}$ -edges at 132 eV (blue), N K-edge at 401 eV (pink) and C K-edge at 284 eV (orange).

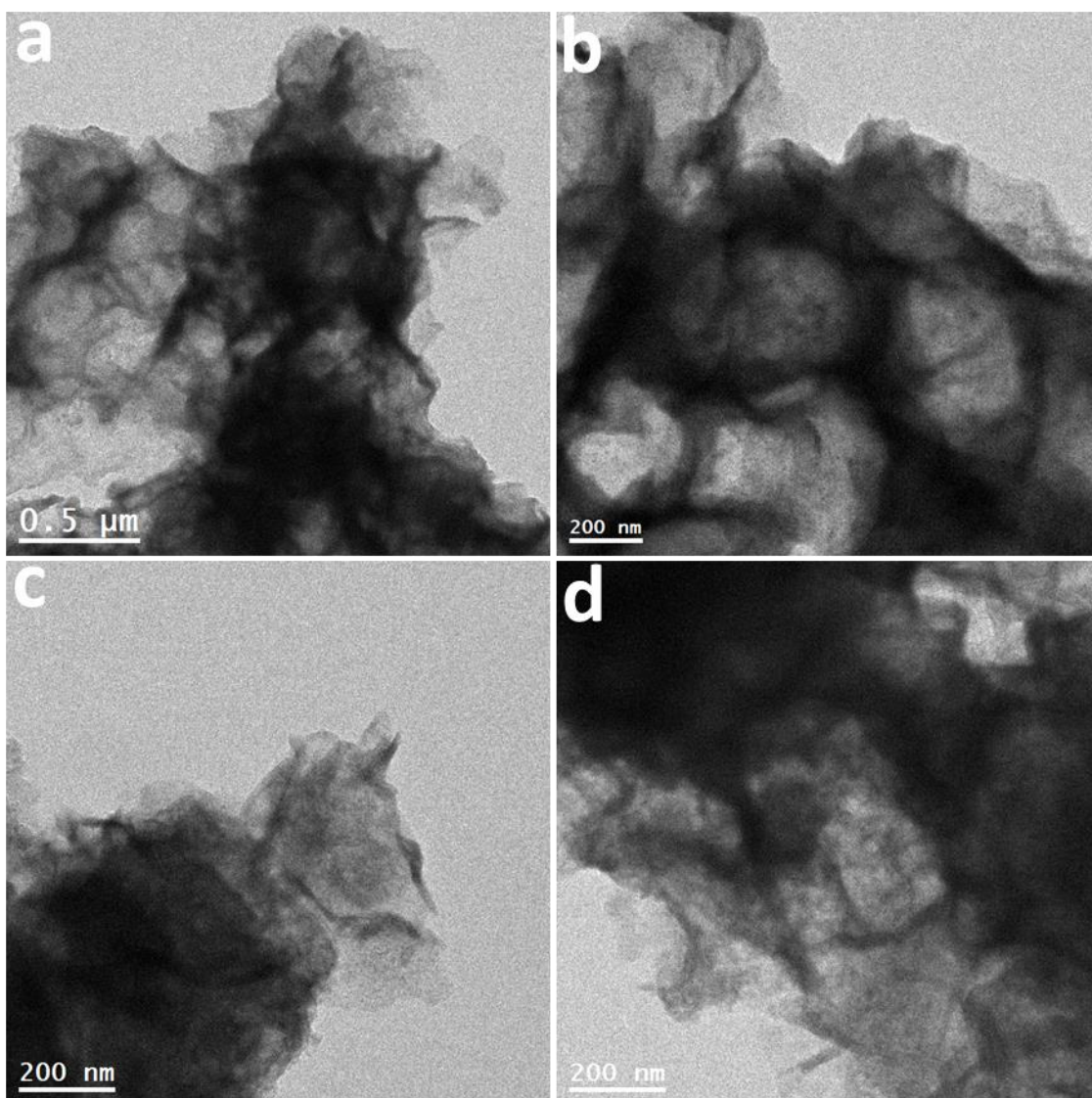


Figure 4.7. a-d) TEM image of CoMoP.

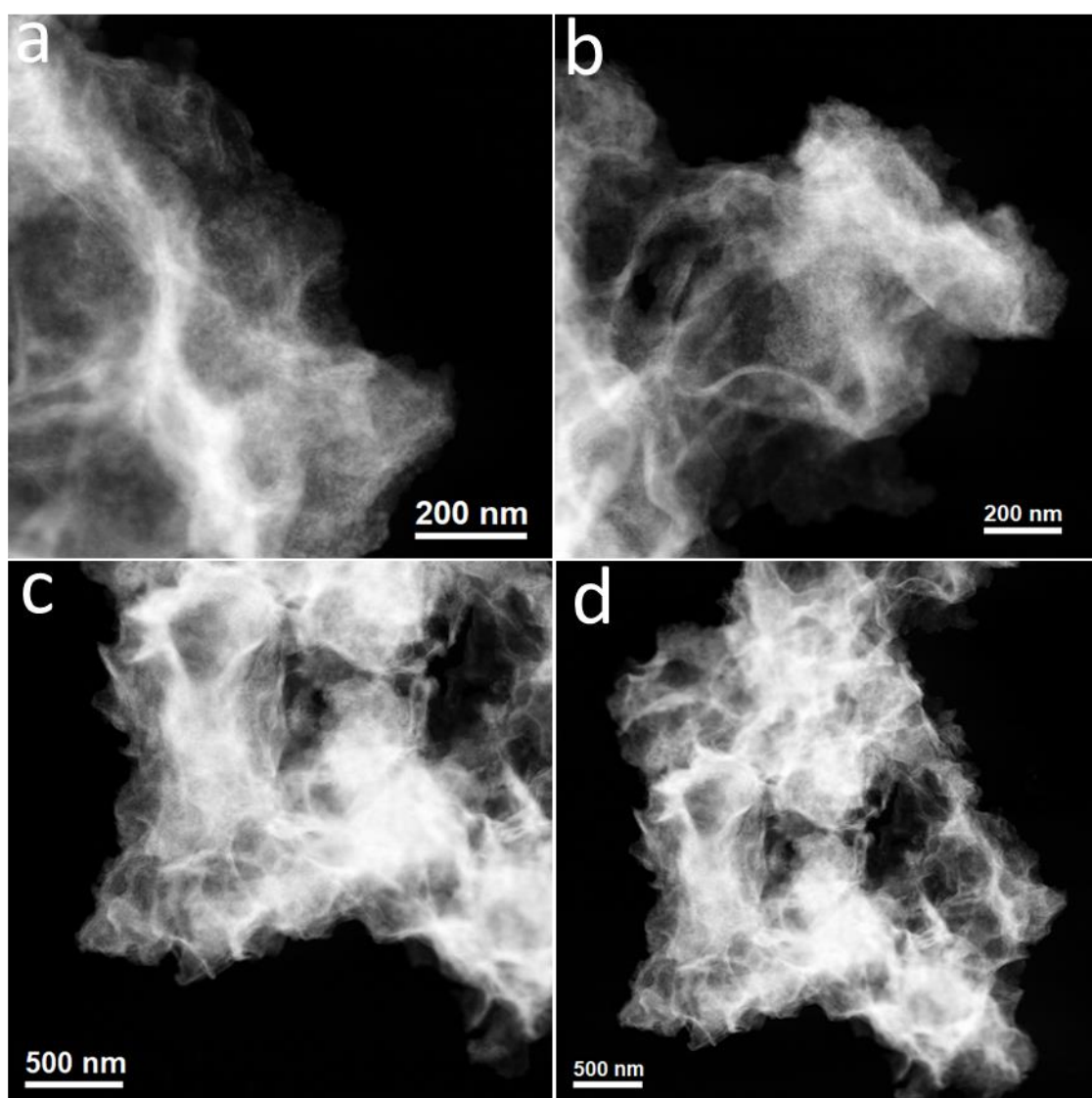


Figure 4.8. a-d) HAADF-STEM micrographs of CoMoP.

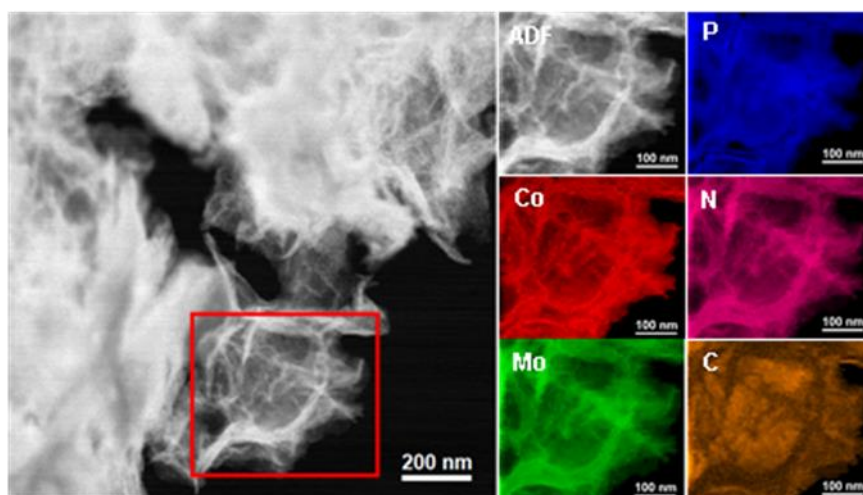


Figure 4.9. EELS chemical composition maps obtained from the red squared area of the STEM micrograph. Individual Co $L_{2,3}$ -edges at 779 eV (red), Mo $M_{4,5}$ -edges at 230 eV (green), P $L_{2,3}$ -edges at 132 eV (blue), N K-edge at 401 eV (pink) and C K-edge at 284 eV (orange).

Figure 4.6a, b and 4.7 displays TEM images of CoMoP, further revealing their ultrathin nanosheet structure. HAADF-STEM analysis and EELS chemical composition maps (Figure 4.6e, 4.8 and 4.9) displayed a homogenous distribution of C, Co, Mo and P within each CoMoP nanosheet. HRTEM images (Figure 4.6c) and SAED patterns (Figure 4.6d) showed CoMoP to present a weak crystallinity, with strong middle/long-range disordered.⁴⁴⁻⁴⁶ In this regard, while the XRD patterns of ZIF-67 and $\text{Na}_2\text{MoO}_4\text{-ZIF-67}$ displayed a good crystallinity (Figure 4.10a), the Co-Mo MOF already presented a mostly amorphous structure. After phosphorization, CoP maintained a relatively well-organized lattice, and CoMoP displayed a weak crystallographic order, consistently with HRTEM results (Figure 4.10b).

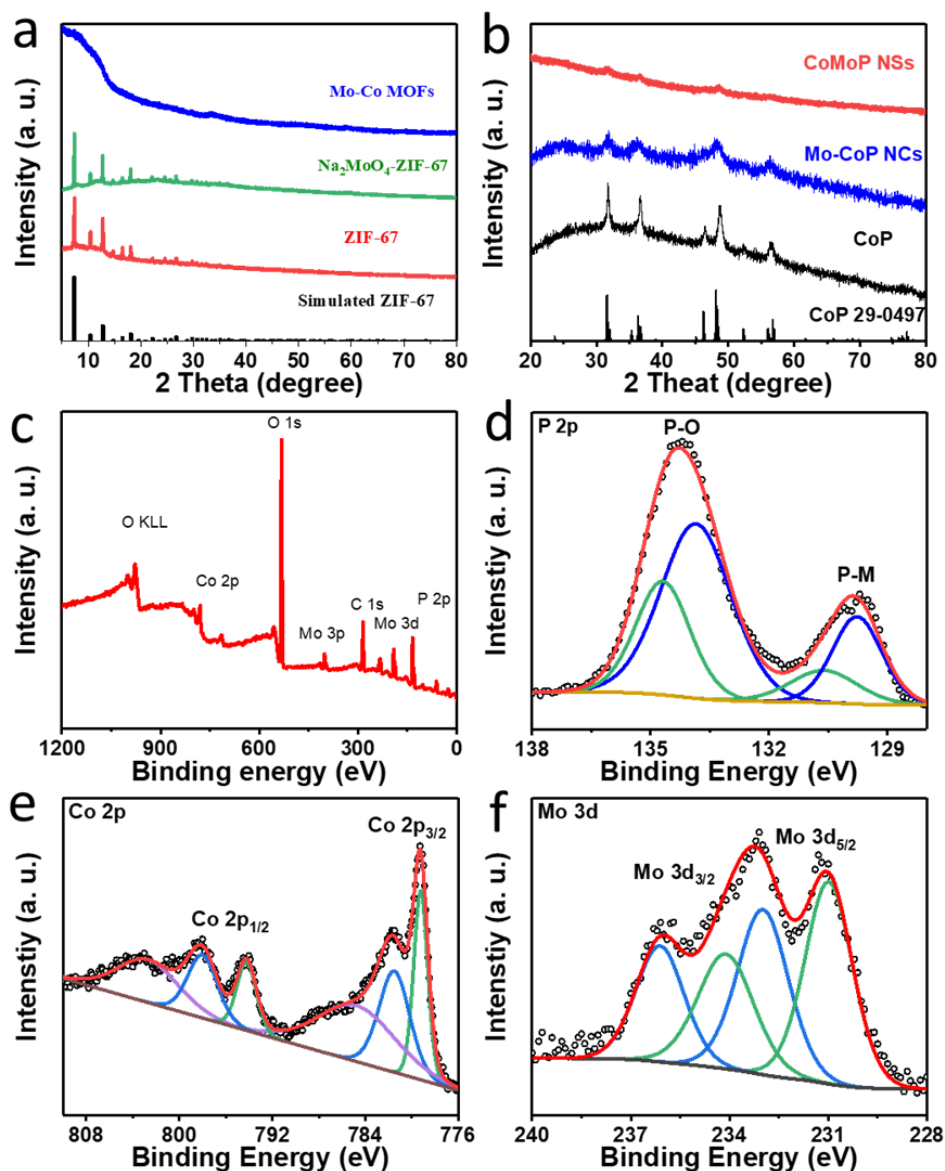


Figure 4.10. (a,b) XRD pattern of the MOFs (a) and the phosphorized materials, CoMoP, Mo-CoP and CoP. (c) XPS survey and high-resolution P 2p (d), Co 2p (e), and Mo 3d (f) XPS spectra of CoMoP.

As expected, the XPS survey spectrum displayed the presence of C, N, O, P, Co and Mo elements on the surface of CoMoP (Figure 4.10c). The high-resolution P 2p XPS spectrum displayed two doublets, which we associated with P within the metal phosphide lattice ($P\ 2p_{3/2} = 129.7\text{ eV}$), and a phosphate chemical environment ($P\ 2p_{3/2} = 133.8\text{ eV}$) (Figure 4.10d).^{41, 47} The Co 2p XPS spectrum displayed six peaks (Figure 4.10e). The main Co 2p contribution was assigned to Co within the phosphide lattice ($Co\ 2p_{3/2} = 779.3\text{ eV}$). A second doublet was associated with Co within an oxide, hydroxide or phosphate chemical environment ($Co\ 2p_{3/2} = 781.5\text{ eV}$). The last two bands were assigned to satellite peaks.^{28-30, 48, 49} Finally, the Mo 3d XPS spectrum displayed two doublets

assigned to Mo within the metal phosphide lattice ($\text{Mo } 3d_{5/2} = 228.2 \text{ eV}$) and an oxidized chemical environment ($\text{Mo } 3d_{5/2} = 233.0 \text{ eV}$) (Figure 3f).⁵⁰⁻⁵²

4.4.2 Oxygen evolution reaction

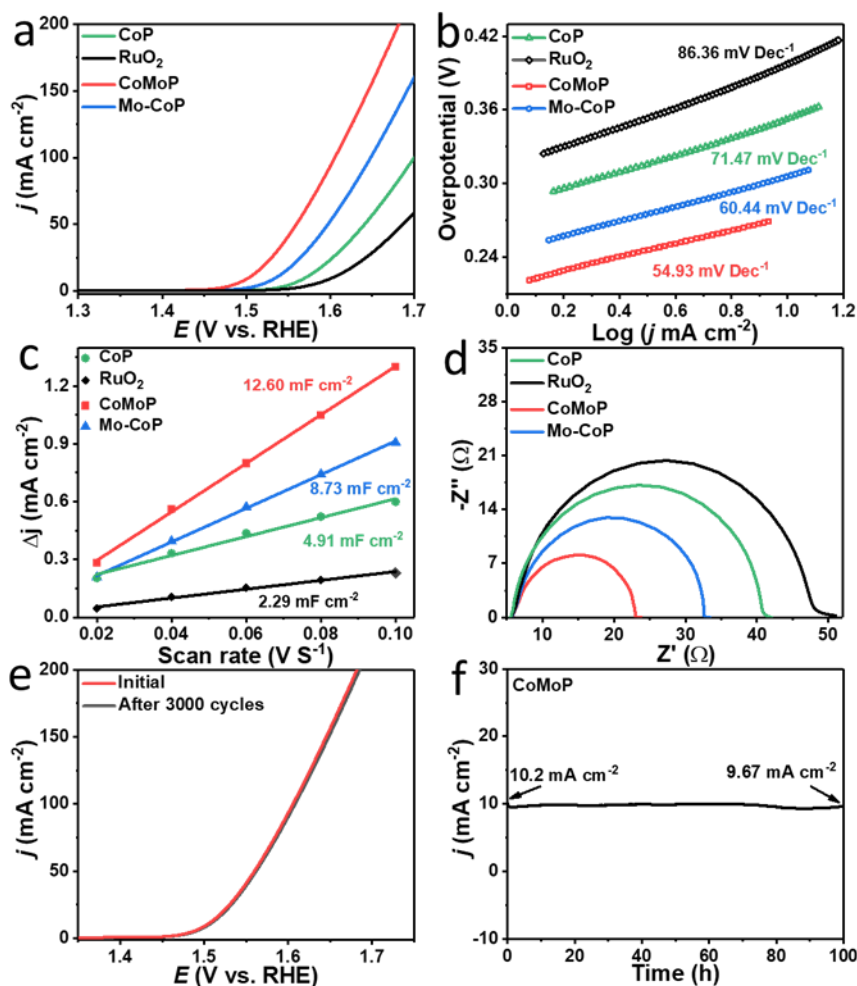


Figure 4.11. a) OER polarization curves in 1.0 M KOH. b) Corresponding Tafel plots. c) Double-layer capacitances (C_{dl}). d) Nyquist plots of the EIS data. e) OER polarization curves before and after 3000 cycles. f) OER chronoamperometric data for CoMoP at an over-potential of 273 mV.

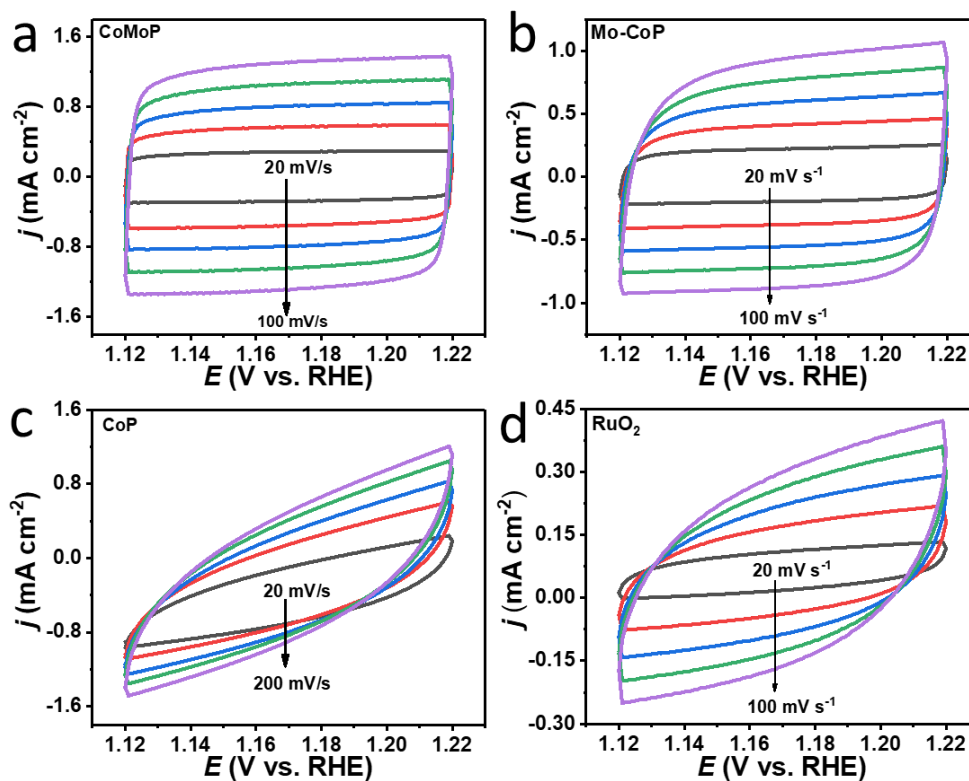


Figure 4.12. Cyclic voltammograms for a) CoMoP; b) Mo-CoP; c) CoP and d) RuO₂ in the non-faradaic region of 1.12-1.22 V vs. RHE at various scan rates.

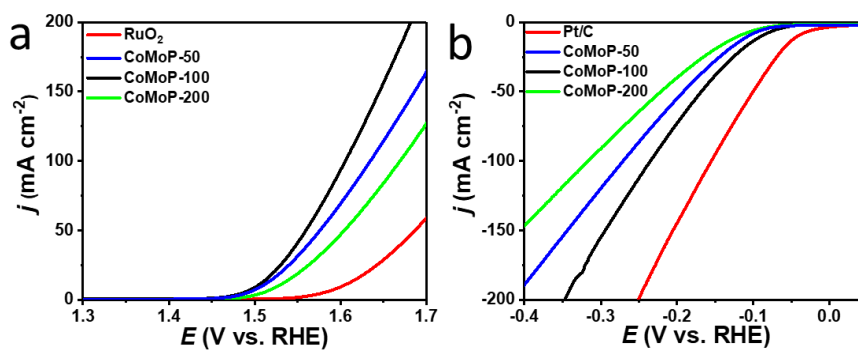


Figure 4.13. a) OER and b) HER polarization curves of CoMoP with different Mo content in 1.0 M KOH.

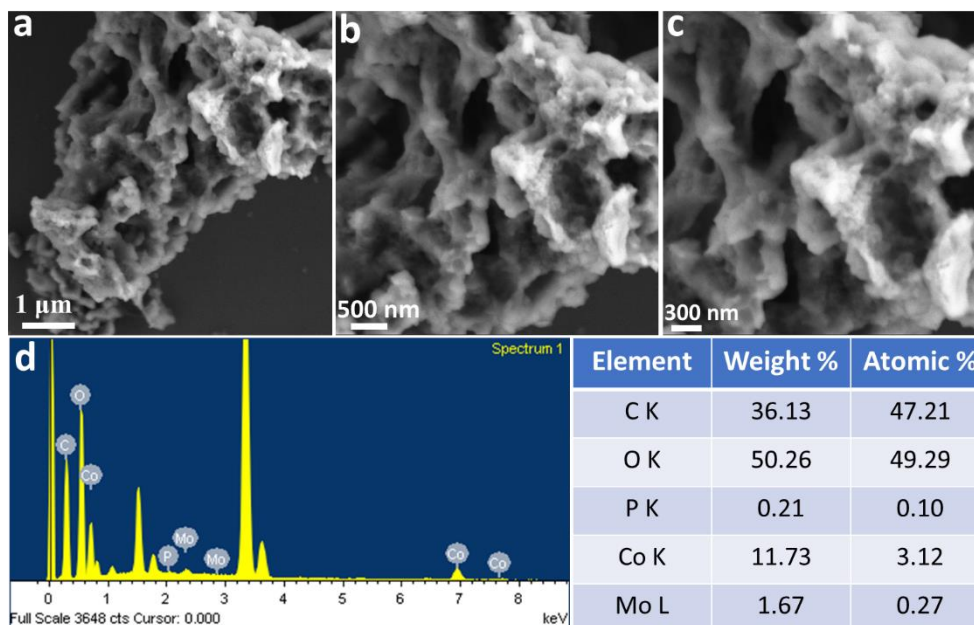


Figure 4.14. a-c) SEM image and d) EDX spectrum of CoMoP after long term OER stability testing.

Table S1. Comparison of OER performance of CoMoP with some previously reported CoP-based catalysts in 1.0 M KOH solution.

Catalysts	Electrolyte	Overpotentials (mV)	Tafel slope (mV/dec)	Reference
CoMoP	1.0 M KOH	273	55	<i>This work</i>
O-CoP nanosheets	1.0 M KOH	310	83	[1]
CoP/NCNHP	1.0 M KOH	310	70	[2]
Mo-CoOOH	1.0 M KOH	302	56	[3]
CoP/CoCr ₂ O ₄	1.0 M KOH	290	52	[4]
CoP PNWs	1.0 M KOH	326	80	[5]
CoP/CNFs	1.0 M KOH	325	29	[6]

The OER activity of CoMoP was evaluated at room temperature using a three-electrode system in 1.0 M KOH alkaline solution. As a reference, Mo-CoP, CoP and a commercial RuO₂ catalyst were also evaluated in the same cell and reaction conditions. The LSV polarization curves displayed the CoMoP to be characterized by an outstanding OER activity, with an overpotential of only 273 mV at a current density of 10 mA cm⁻² (Figure 4.11 and 4.13a). This overpotential is well below that of Mo-CoP, CoP and the RuO₂

electrocatalyst tested here and outperforms that of previously reported CoP-based OER catalysts, as shown in Table S1. As displayed in Figure 4b, CoMoP was not only characterized by the lowest overpotential at 10 mA cm^{-2} , but also provided the lowest Tafel slope, 54.9 mV dec^{-1} . This value was significantly below that of Mo-CoP (60.4 mV dec^{-1}), CoP (71.5 mV dec^{-1}) and RuO_2 (86.4 mV dec^{-1}), which indicates CoMoP to have associated a faster OER reaction kinetics.^{53, 54}

The electrochemical active areas (ECSA) of CoMoP, Mo-CoP NCs, CoP and RuO_2 were estimated according to the double-layer capacitance (C_{dl}) determined via CV in the non-faradaic region at different scan rates, 20, 40, 60, 80, and 100 mV s^{-1} (Figures 4.12 and 4.11c). CoMoP displayed larger C_{dl} (12.6 mF cm^{-2}) than Mo-CoP (8.7 mF cm^{-2}), CoP (4.9 mF cm^{-2}) and RuO_2 (2.3 mF cm^{-2}). This result indicates that CoMoP offers a higher density of accessible electrochemical active sites, which we relate to the proper composition and nanosheet structure of CoMoP.

The charge transport/transfer ability of the electrocatalysts was evaluated by electrochemical impedance spectroscopy (EIS). An equivalent circuit model including a charge transfer resistance (R_{ct}) and a solution resistance (R_s) during the OER process was used to fit the Nyquist plots displayed in Figure 4.11d.^{55, 56} CoMoP exhibited the smallest R_{ct} (17.99Ω), well below that of Mo-CoP ($R_{ct} = 27.90 \Omega$), CoP ($R_{ct} = 36.70 \Omega$) and RuO_2 (45.47Ω). These results reveal the CoMoP nanosheets to enable a faster charge transfer at the electrode/electrolyte interfaces, thus accelerating the OER electrocatalytic kinetics.

The long-term stability of CoMoP was further analyzed by CV and chronopotentiometry measurements.^{57, 58} Figure 4.11e shows how the LSV curve of CoMoP after 3000 CV cycles closely resembles that of the first cycle. The chronoamperometry test displayed CoMoP to have an outstanding long-term catalytic activity with just a 3% current density decay after 100 h of operation at 273 mV (Figure 4.11f). The morphology and structure of post-catalysts after long term stability shown in Figure 4.14, we can find the ultrathin nanosheet of CoMoP transform into layered structure. Meanwhile, the EDX result shown the content of Mo and P massive loss. These results demonstrate that the structure of the catalyst is re-organized into metal (oxy)-hydroxide during the OER reaction, which is also consistent with some reports in the literature.^{59, 60}

4.4.3 Hydrogen evolution reaction

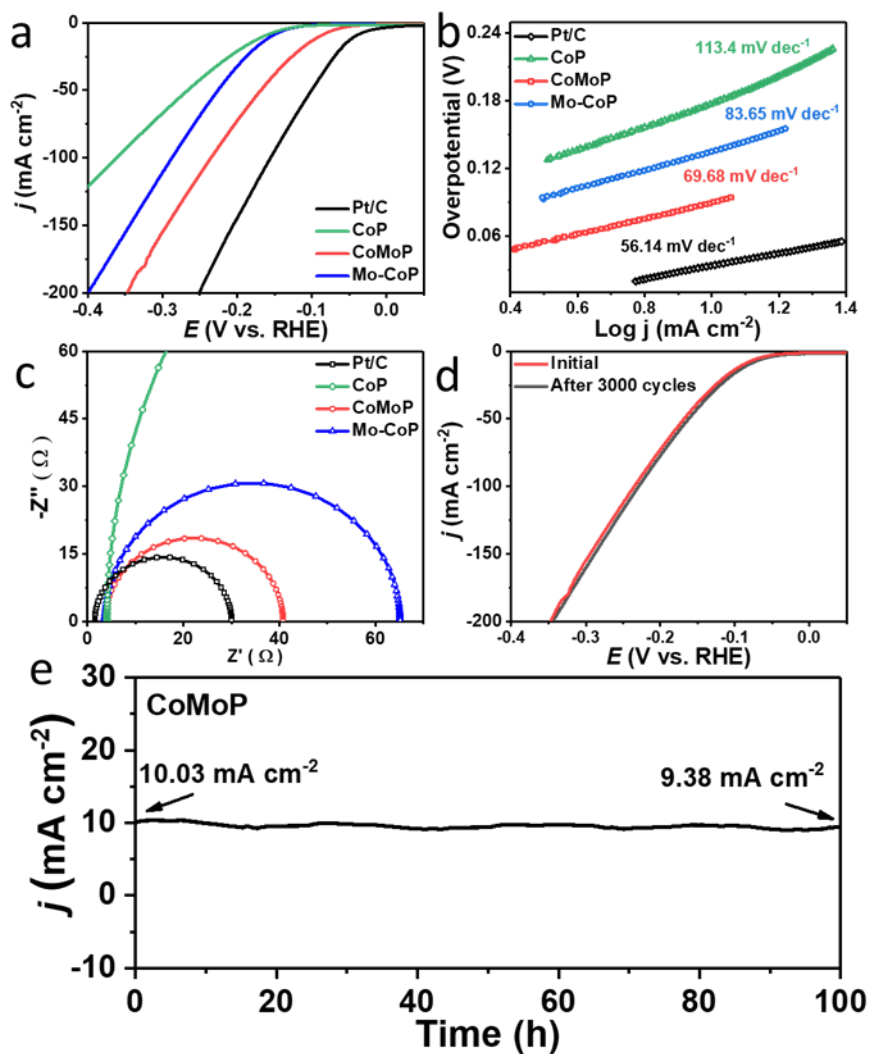


Figure 4.15. a) HER polarization curves in 1.0 M KOH. b) Corresponding Tafel plots. c) Nyquist plots of the EIS data. d) HER polarization curves before and after 3000 cycles. e) Chronoamperometry data for CoMoP at the 89 mV overpotential.

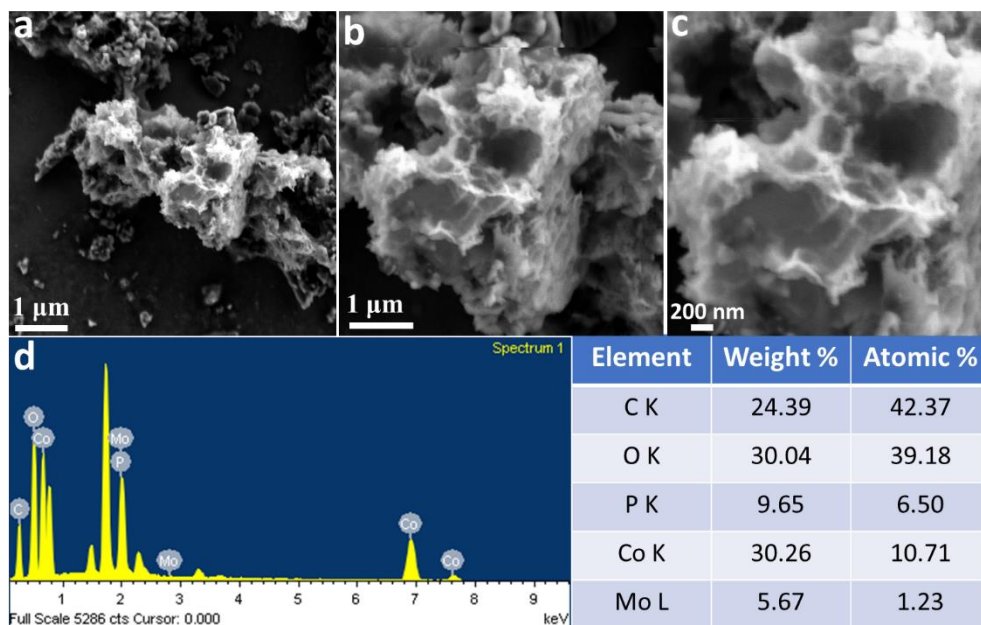


Figure 4.16. a-c) SEM image and d) EDX spectrum of CoMoP after long term HER stability testing.

Table S2. Comparison of HER performance of CoMoP with some previously reported CoP-based catalysts in 1.0 M KOH solution.

Catalysts	Electrolyte	Overpotentials (mV)	Tafel slope (mV/dec)	Reference
CoMoP	1.0M KOH	89	70	<i>This work</i>
NiFeP@N-CS	1.0 M KOH	186	112	[7]
NiCo-P	1.0 M KOH	169	68	[8]
Ni _{0.85} Se/RGO	1.0 M KOH	169	65	[9]
NCT@CoP@MoS ₂	1.0 M KOH	195	74	[10]
Ce ₁ -CoP	1.0 M KOH	144	70	[11]
V-doped CoP	1.0 M KOH	235	91	[12]

The HER performance of CoMoP was evaluated in 1.0 M KOH using a three-electrode system and it was compared with that of Mo-CoP, CoP and a commercial Pt/C catalyst. As shown in Figure 4.155a and 4.13b, the CoMoP electrocatalyst displayed a relatively low HER overpotential of 89 mV at the current density of 10 mA cm⁻², slightly above that of Pt/C (42 mV), and well below that of Mo-CoP (154 mV), CoP (165 mV) and most previously reported phosphide-based HER electrocatalysts (Table S2). The Tafel slope of CoMoP (69.7 mV dec⁻¹) was also much lower than those of Mo-CoP (83.7 mV dec⁻¹), CoP (113.4 mV dec⁻¹) and close to that of Pt/C (56.1 mV dec⁻¹) (Figure 4.15b), which

indicated rapid HER reaction kinetics following the Volmer–Heyrovsky mechanism.^{61, 62} CoMoP also displayed the smallest semicircular diameter in the Nyquist plot of the EIS data among the phosphide catalysts tested (Figure 4.15c), showing the lowest charge transfer resistance during catalytic processes. In terms of stability under HER conditions, Figure 4.15d displays how CoMoP suffered a very minor change of the LSV curves after 3000 cycles. Besides, CA measurement showed the current density to decrease just 6% after 100 h of continuous operation under HER conditions at an overpotential 89 mV (Fig. 4.15e). The Morphology and EDX result after long time HER were shown in Figure 4.16, which is not much change compared to before reaction. This result indicates that the CoMoP is very stable during the HER process.

4.4.4 Overall water splitting

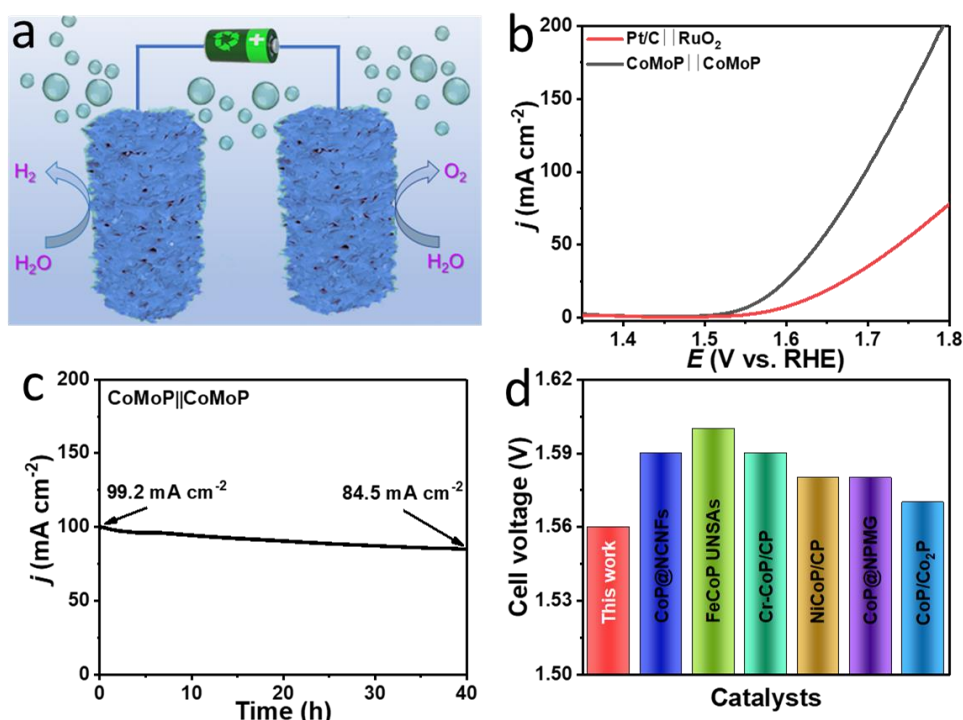


Figure 4.17. a) Schematic diagram of the OWS in a two-electrode system. b) Polarization curves of OWS cells with the electrode pairs: CoMoP||CoMoP and Pt/C||RuO₂ in 1.0 M KOH. c) Chronoamperometric curve of CoMoP in the two-electrode system at 1.70 V polarization. d) Comparison of the CoMoP overpotential at 10 mA cm⁻² with previously reported catalysts in 1.0 M KOH.

Table S3. Comparison of OWS performance of CoMoP with some previously reported CoP-based catalysts in 1.0 M KOH solution.

Catalysts	Electrolyte	Potentials (V)	Reference
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CoMoP	1.0 M KOH	1.56	<i>This work</i>
FeCoP UNSAs	1.0 M KOH	1.60	[13]
Cr-CoP/CP	1.0 M KOH	1.59	[14]
V-CoP@a-CeO ₂	1.0 M KOH	1.56	[15]
NiCoP	1.0 M KOH	1.58	[16]
CoP-N/Co foam	1.0 M KOH	1.61	[17]
CoP@NPMG	1.0 M KOH	1.58	[18]
CoP/Co ₂ P	1.0 M KOH	1.57	[19]

Owing to the excellent OER and HER performances demonstrated by CoMoP, a two-electrode configuration electrolyzer with CoMoP both as the positive and negative electrodes was constructed and tested for OWS in 1.0 M KOH solution. As shown from the polarization curves displayed in Figure 4.17b, the assembled device just required a cell volt-age of 1.56 V to reach a current density of 10 mA cm^{-2} , which is significantly below that of a cell containing Pt/C and RuO₂ electrodes (1.61 V). More importantly, after 40 h of continuous operation, the CoMoP-based cell still maintained an outstanding performance, with just a 14.8% loss at high current density (Figure 4.17c). Thus, the as-prepared CoMoP can be considered as a highly competitive electrocatalytic catalyst for OWS compared with the previously reported OWS catalysts (Figure 4.17d, Table S3). Besides, its outstanding stability demonstrates its potential for large-scale hydrogen production from water splitting.

4.5 Conclusions

In conclusion, ultrathin CoMoP nanosheets were engineered using the Co-MOF ZIF-67 as a self-sacrificial template and ammonium molybdate as a shape-defining agent and Mo source. CoMoP nanosheets exhibited outstanding performance towards HER and OER in alkaline media, which we associate with the proper transport properties and elec-tronic energy levels provided by their composition and their porous nanosheet structure. In particular, CoMoP presented low overpotentials of 89 and 273 mV at a current density of 10 mA cm^{-2} for HER and OER, respectively. Furthermore, CoMoP electrocatalysts also showed excellent long-term stabilities in alkaline electrolyte, with a minor current density decrease after 100 h continuous operation. When used for OWS, a cell voltage of only 1.56 V was needed to reach a current density of 10 mA cm^{-2} . This work provides a suitable strategy to synthesize high-performance Co-Mo-P electrocatalysts with abundant exposed

active sites and effective avenues for charge and electrolyte transport, and it can be employed to further tune the structure and composition of other 2D nanostructures with optimized performance towards OWS and other electrocatalytic reactions.

4.6 References

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Chapter 5

Electrochemical Reforming of Ethanol with Acetate Co-Production on Nickel Cobalt Selenide Nanoparticles

5.1 Abstract

The energy efficiency of water electrolysis is limited by the sluggish reaction kinetics of the anodic oxygen evolution reaction (OER). To overcome this limitation, OER can be replaced by a less demanding oxidation reaction, which in the ideal scenario could be even used to generate additional valuable chemicals. Herein, we focus on the electrochemical reforming of ethanol in alkaline media to generate hydrogen at a Pt cathode and acetate as a co-product at a $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$ anode. We first detail the solution synthesis of a series of $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$ electrocatalysts. By adjusting the Ni/Co ratio, the electrocatalytic activity and selectivity for the production of acetate from ethanol are optimized. Best performances are obtained at low substitutions of Ni by Co in the cubic NiSe_2 phase. Density function theory reveals that the Co substitution can effectively enhance the ethanol adsorption and decrease the energy barrier for its first step dehydrogenation during its conversion to acetate. However, we experimentally observe that too large amounts of Co decrease the ethanol-to-acetate Faradaic efficiency from values above 90% to just 50 %. At the optimized composition, the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ electrode delivers a stable chronoamperometry current density of up to 45 mA cm^{-2} , corresponding to 1.2 A g^{-1} , in a 1 M KOH + 1 M ethanol solution, with a high ethanol-to-acetate Faradaic efficiency of 82.2% at a relatively low potential, 1.50 V vs. RHE, and with an acetate production rate of $0.34 \text{ mmol cm}^{-2} \text{ h}^{-1}$.

5.2 Introduction

Molecular hydrogen is a convenient carbon-free energy carrier and a key component in the chemical industry. While molecular hydrogen does not exist in nature, it can be produced by water electrolysis using renewable energy sources such as wind, hydropower, and solar.¹ However, while water electrolysis systems have been commercialized for several years, their high cost has prevented extensive deployment, and most molecular hydrogen is still being produced by the partial oxidation and steam reforming of natural gas and coal gasification.² To turn this trend around, cost-effective strategies for the production of hydrogen from renewable sources need to be developed. In this context, biomass-derived products provide an excellent alternative source of hydrogen owing to

their renewable character and their net-zero CO₂ footprint.³ Besides, the partial oxidation of an organic molecule offers a less energy demanding anodic oxidation reaction, which can contribute to overcoming the energy efficiency limitation of water electrolysis associated with the sluggish reaction kinetics of the oxygen evolution reaction (OER).⁴⁻⁶ An additional advantage of the production of hydrogen from the reforming of waste or biomass-derived organics is the potential co-generation of valuable organic chemicals, which can both improve process economics and further diminish the dependence on fossil resources that are currently used to produce them.⁷⁻⁹ On top of these advantages, the replacement of OER by an organic oxidation reaction enables the implementation of coupled cost-effective waste abatement processes. Thus, overall, the clean electrochemical conversion of organic waste and biomass-derived products into value-added chemicals driven by renewable energy has both high fundamental interest and enormous potential for socio-economic and environmental impact.¹⁰⁻¹³

In this scenario, (bio)ethanol is a paradigmatic and particularly interesting hydrogen source. Ethanol is a key commodity in the chemical industry, used as a precursor or building block for the synthesis of a plethora of chemicals, including formaldehyde, acetic acid, and plastics.^{14,15} Ethanol can be renewably generated from the reduction of CO₂ and several biomass-derived feedstocks and organic residues such as sewage sludge.¹²⁻¹⁴ As a liquid, ethanol can be easily stored and transported. Besides, bioethanol aqueous solutions can be directly used in electrocatalytic processes, without the need for purification. Compared with water splitting, the production of hydrogen from ethanol is thermodynamically advantageous ($\Delta G^0 = +237 \text{ kJ}\cdot\text{mol}^{-1}$ for water oxidation vs. $\Delta G^0 = +9.6 \text{ kJ}\cdot\text{mol}^{-1}$ for ethanol oxidation to acetate), which decreases the energy input required.¹⁶ The reforming of ethanol also prevents the H₂ and O₂ back reaction. Besides, compared with the complete ethanol reforming down to CO₂, the production of H₂ and acetate could have higher economical profitability associated with the high economic value of acetate as a side product.¹⁷

In terms of catalysts, while OER generally requires high-cost noble metal electrocatalysts, the electrooxidation of organic molecules, such as methanol or ethanol, in alkaline media can be activated at a lower cost using abundant 3d transition metal-based electrocatalysts, e.g. nickel, iron and cobalt.¹⁷⁻¹⁹ To improve the electrocatalytic performance, multimetallic transition metal-based nanoparticles have been also

developed and studied. Among them, nickel-cobalt compounds have demonstrated particularly high activity towards OER,^{20–22} and excellent performance for the conversion of methanol to formate.^{23–26} Thus, we hypothesize nickel-cobalt selenides to be excellent electrocatalysts for the ethanol oxidation catalysts, but this reaction and its mechanism is yet to be studied on these materials.

Herein, we detail the preparation of bimetallic Ni-Co selenides nanoparticles (NPs) over a full range of compositions using a solution-based strategy. This set of materials is tested for the partial electrooxidation of ethanol in an alkaline electrolyte. Finally, the material is optimized to minimize the overpotential and maximize the activity and Faradaic efficiency for ethanol to acetate conversion.

5.3 Experimental Section

5.3.1 Chemicals

All chemicals, including cobalt(II) acetylacetonate ($\text{Co}(\text{acac})_2$, 97%, Sigma Aldrich), selenium powder (Se, 200 mesh, 99.5%, Acros Organics), nickel(II) acetylacetonate ($\text{Ni}(\text{acac})_2$, 96%), oleylamine (OAm, $\text{C}_{18}\text{H}_{37}\text{N}$, 80-90%, Acros Organics), potassium hydroxide (KOH, 85%, Sigma Aldrich), potassium carbonate (K_2CO_3 , 99.5%, Sigma Aldrich), potassium bicarbonate (KHCO_3 , 99.7%, Sigma Aldrich), 1,2-ethanedithiol (EDT, $\text{HSCH}_2\text{CH}_2\text{SH}$, 98%, Sigma Aldrich), oleic acid (OAc, $\text{C}_{18}\text{H}_{34}\text{O}_2$, 99%, Sigma Aldrich), carbon black (CB, Vulcan XC72, Sigma Aldrich), and Nafion (10 wt.%, perfluorinated ion-exchange resin, dispersion in water, Sigma Aldrich), were used as received, without further treatment. Analytical grade chloroform and ethanol for the washing process were obtained from various sources. MilliQ water ($18.2 \text{ M}\Omega\cdot\text{cm}$) was used for electrolyte and ink preparation, and ion chromatography (IC) measurements. An argon-filled glove box was used to handle sensitive chemicals and for ink preparation.

5.3.2 Solution-based synthesis of $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$ NPs

Bimetallic selenide NPs were produced from a two-step process involving the preparation of a reactive ink and its decomposition. First, the precursor ink was prepared inside an argon-filled glove box by dissolving $(1-x)$ mM of $\text{Ni}(\text{acac})_2$, x mM of $\text{Co}(\text{acac})_2$, and 8 mM of Se powder inside a vial with 30 mL of OAm and 3 mL of EDT under vigorous stirring for 1h at 50°C . The introduction of EDT was required to dissolve the Se powder.

The obtained solution was then filtered through a 0.2 μm filter. Then, 36 mL of the prepared precursor together with 60 mL of OAm and 30 mL OAc were placed in a 250 mL three-neck flask and vacuumed at 60 $^{\circ}\text{C}$ for 30 min followed by heating to 220 $^{\circ}\text{C}$ under Ar at a rate of 5 $^{\circ}\text{C min}^{-1}$. After reacting for 20 min, the solution was rapidly cooled down to room temperature in a water bath. Next, the crude solution was mixed with 60 mL of chloroform and then centrifuged at 8000 rpm for 5 min. The washing process was repeated by dispersion in chloroform/ethanol and centrifugation several times. Finally, the obtained product was stored in chloroform and stored in the glovebox.

5.3.3 Material characterization

Laboratory X-ray diffraction (XRD) was performed on a Bruker AXS D8 Advance (Cu K radiation: $\lambda = 1.5106 \text{ \AA}$) to study the crystal structure. Scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) measurements were conducted on a Gemini 300 field emission scanning electron microscope (Zeiss, Germany) equipped with an AZtecOne UltimMax40 energy spectrometer. High-resolution transition electron microscopy (HRTEM) and scanning TEM (STEM) investigation were performed on a field emission gun FEI Tecnai F20 microscope. High angle annular dark-field (HAADF) STEM was combined with electron energy loss spectroscopy (EELS) in the Tecnai microscope using a Gatan Quantum filter. The materials' pore size distribution and specific surface area were analyzed by means of N_2 adsorption on a ASAP 2460 Micromeritics system. Specific surface areas were determined by means of the Brunauer–Emmett–Teller (BET) approach, considering equally spaced points in the P/Po range. The pore size distribution was calculated from the isotherms desorption branches using the Barrett–Joyner–Halenda (BJH) model. X-ray photoelectron spectroscopy (XPS) analyses were conducted on a Specs system.

5.3.4 Electrochemical Measurements

Electrochemical tests were carried out on a Bio-logic SP-200 potentiostat using a conventional three-electrode system including a Pt wire as the counter electrode, a Hg/HgO reference electrode, and the $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$ NPs supported on CB on top of a 5 mm diameter glassy carbon (GC) as working electrode (WE). To prepare the WE, a catalytic ink was prepared by dispersing 3 mg of dried NPs and 6 mg of CB in a vial containing 1.8 mL of MilliQ water/ethanol (v/v = 1:1) and 100 μL of a 10 wt% Nafion solution,

followed by half-an-hour of vigorous sonication. Afterwards, 5 μL of this ink were drop-casted on a carefully polished GC electrode and dried naturally in air. Before the measurement, the alkaline electrolyte was bubbled with high-purity N_2 gas for half an hour. Cyclic voltammetry (CV) and chronoamperometry (CA) were applied to study the electrocatalytic performance. To analyze the product of the oxidation reaction at the anode and calculate the ethanol-to-acetate faradaic efficiency, 0.5 mL of the solution was collected, diluted 20-fold with MilliQ water, and then analyzed by IC. A freshly prepared 4.5 mM KCO_3 and 0.8 mM KHCO_3 solution was used as leachate solution for the measurement. The amount of product was quantified with a standard curve obtained from known acetate concentrations. At the cathode, the generated hydrogen was determined by gas chromatography (GC, 8890, Agilent Technologies) connected to the electrocatalytic cell. Before measurement, a stable flow rate of 20 $\text{cm}^3 \text{ min}^{-1}$ Ar (99.999%) was bubbled for 30 mins at the Pt wire in an H-type two-compartment cell, which is separated by a Nafion-115 proton membrane. The GC product analysis was conducted every 12 mins. The produced gas was identified and quantified by a calibration curve using known concentrations of standard H_2 gas. All obtained potentials (vs. Hg/HgO) were converted to the reversible hydrogen electrode (RHE) reference according to the Nernst equation: $E_{\text{RHE}} = E_{\text{Hg}/\text{HgO}} + 0.059 \times \text{pH} + E_{\text{Hg}/\text{HgO}}^\ominus$, where $E_{\text{Hg}/\text{HgO}}$ is the measured potential, $E_{\text{Hg}/\text{HgO}}^\ominus$ is the reference potential of 0.098 V, and pH is 13.6 as it corresponds to the 1.0 M KOH solution. All current densities were referred to the geometrical area of the GC electrode, i.e. 0.196 cm^2 .

5.3.5 Computational method

The Vienna ab initio package (VASP) was used to perform all the density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the PBE formulation.^{27–29} The projected augmented wave (PAW) potential was used to describe the ionic cores and valence electrons were taken into account using a plane wave basis set with a kinetic energy cutoff of 400 eV.^{30,31} Partial occupancies of the Kohn–Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than 10^{-5} eV. A geometry optimization was considered convergent when the force change was smaller than 0.02 eV/Å. Grimme’s DFT-D3 methodology was used to describe the dispersion interactions.³²

Using a $7 \times 11 \times 9$ Monkhorst-Pack k-point grid for Brillouin zone sampling, the equilibrium lattice constants of the monoclinic NiOOH unit cell were optimized to be $a=5.168 \text{ \AA}$, $b=2.847 \text{ \AA}$, $c=4.516 \text{ \AA}$, at $\alpha=90^\circ$, $\beta=107.1^\circ$, $\gamma=90^\circ$. They were used to construct a NiOOH(001) surface model (model 1) with $p(2 \times 3)$ periodicity in the x and y directions and 1 stoichiometric layer in the z direction separated by a vacuum layer in the depth of $15 \text{ \AA}$ to separate the surface slab from its periodic duplicates. In another model (model 2), three Co atoms were doped into model 1 by replacing three Ni atoms. One O atom was removed from both models to create an oxygen vacancy. During structural optimizations, the gamma point in the Brillouin zone was used for k-point sampling, and all atoms were allowed to relax.

The free energy of a gas phase molecule or an adsorbate on the surface was calculated by the equation $G = E + \text{ZPE} - TS$, where E is the total energy, ZPE is the zero-point energy, T is the temperature in kelvin (298.15 K), and S is the entropy.

5.4 Results and Discussion

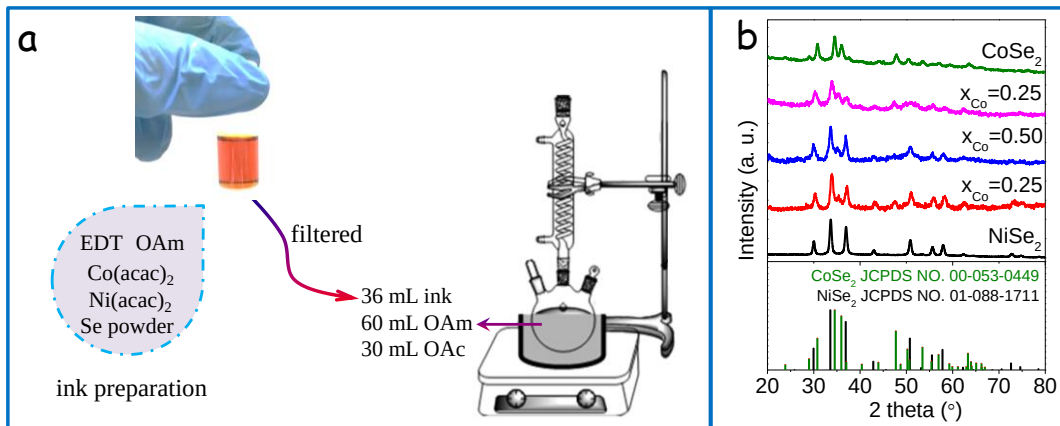


Figure 5.1. (a) Schematic drawing of the solution-based process used to produce Ni_{1-x}Co_xSe₂ NPs. (b) XRD pattern of the as-synthesized product.

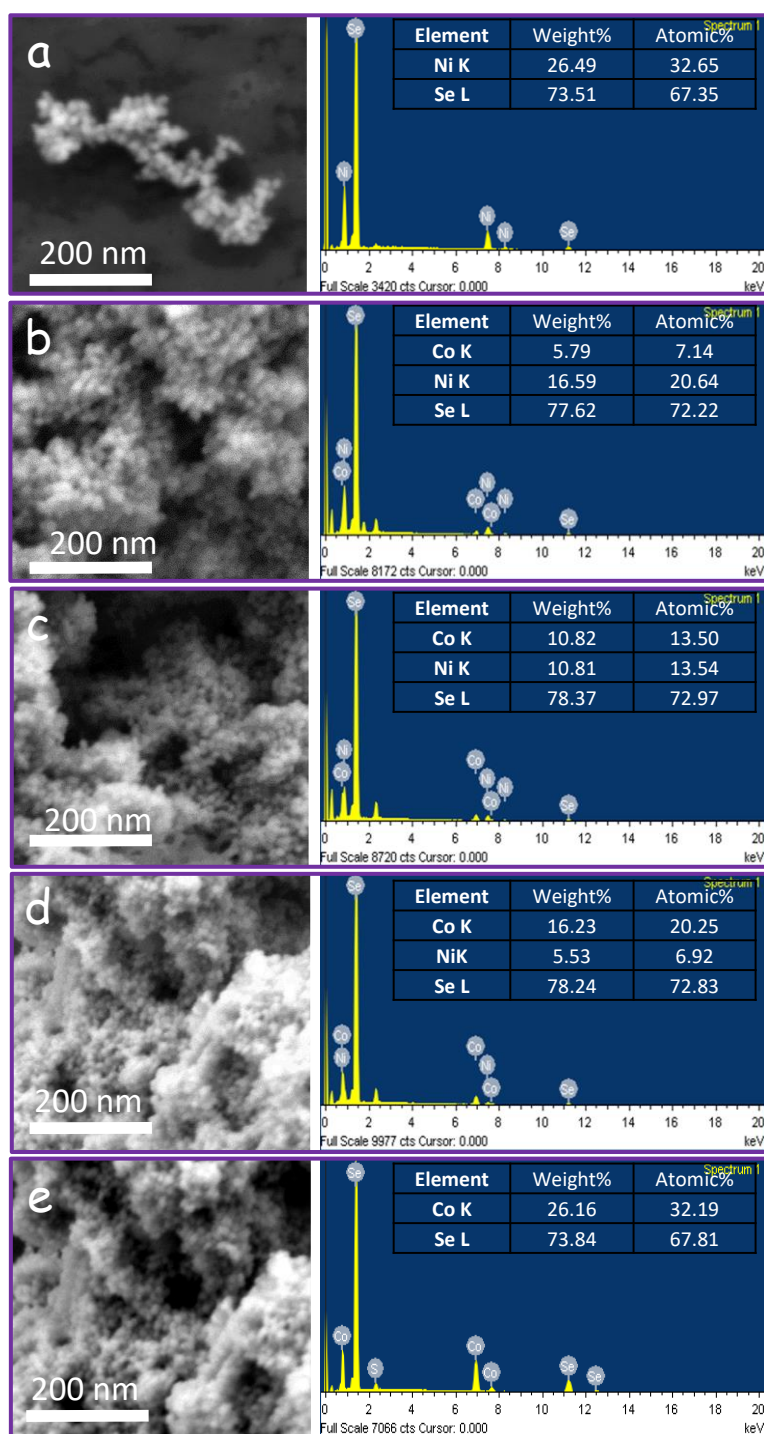


Figure 5.2. SEM-EDS measurement for the $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$ samples with nominal composition (a) $x=0$; (b) $x=0.25$; (c) $x=0.50$; (d) $x=0.75$; (e) $x=1.0$;

$\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$ NPs were produced through a two-step process involving the preparation of a reactive ink from the dissolution of Se and the proper amount of Ni and Co precursors in EDT and OAm and its posterior reaction (see the experimental section for details and Figure 5.1a). Figure 5.1b displays the XRD patterns of the obtained $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$, with

$0 \leq x \leq 1$. For $x=0$ and $x=1$, the crystal structures of NiSe_2 and CoSe_2 could be properly indexed with the cubic $pa-3$ (JCPDS No. 01 088 1771) and the orthorhombic pnm (JCPDS No. 00 053 0449) phases, respectively. With increasing amounts of Co within the NiSe_2 structure, a continuous transition from the cubic NiSe_2 phase to the orthorhombic CoSe_2 structure was observed. Within the experimental error, SEM-EDS analyses showed the composition of the obtained materials to be consistent with the nominal Ni/Co ratios (Figure 5.2). Thus, in the following, we refer to the different samples using the nominal values.

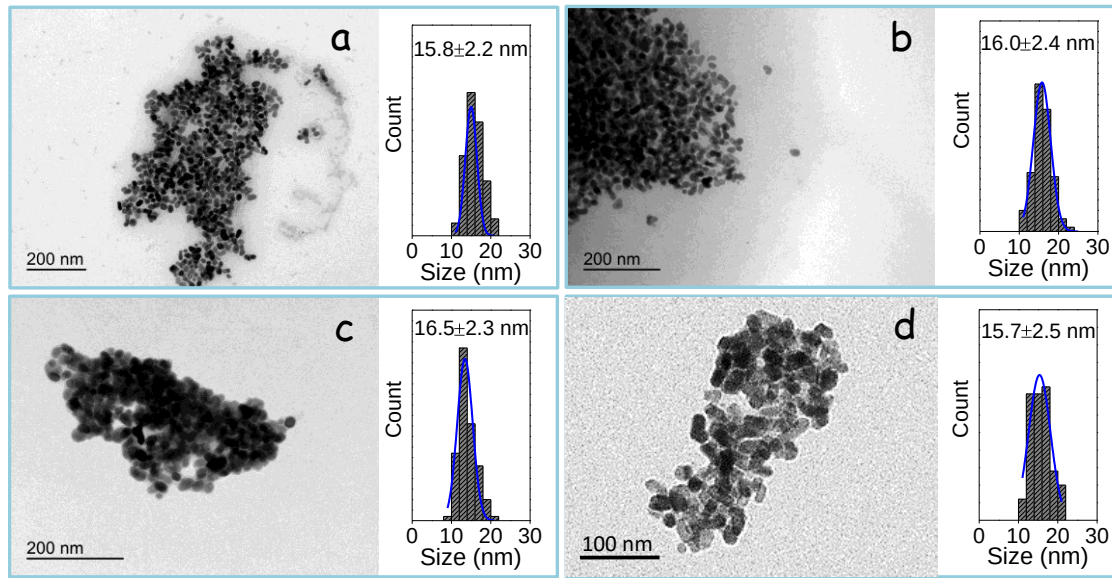


Figure 5.3. TEM micrograph and size distribution histograms of $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$ samples with nominal composition (a) $x=0$; (b) $x=0.50$; (c) $x=0.75$; (d) $x=1.0$;

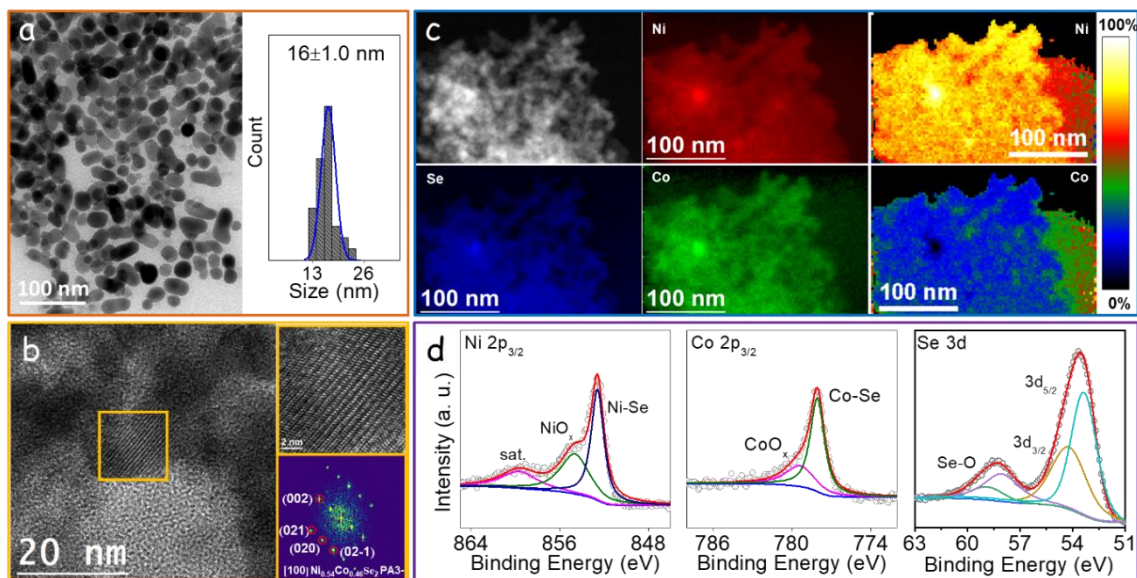


Figure 5.4. TEM and XPS characterization of $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ NPs. (a) TEM image and size distribution histogram. (b) HRTEM micrograph and indexed power spectra. (c) HAADF STEM image and EELS-STEM compositional maps obtained from HAADF STEM shown region. Individual Ni $L_{2,3}$ -edges at 855 eV (red), Co $L_{2,3}$ -edges at 779 eV (red), and Se M_1 -edges at 231 eV (blue) composition maps. Colour gradient maps display the relative compositions of Ni and Co. The colour scale is the same for both panels (Ni and Co). (d) Ni $2p_{3/2}$, Co $2p_{3/2}$, and Se 3d high resolution XPS spectra.

Figure 5.4a displays a representative TEM micrograph of the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ sample. It consists of NPs having an average diameter of around 16 nm. When varying the Co composition over the entire Ni/Co range, the NPs size remained unchanged (Figure 5.3). HRTEM micrographs show the NPs to be highly crystalline (Figure 5.4b). The lattice parameter of the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ NPs is $a=b=c=5.840$ Å, which is in between that of the NiSe_2 cubic phase ($a=b=c=5.973$ Å) and the CoSe_2 cubic phase ($a=b=c=5.681$ Å), in good agreement with a lattice containing a mixture of both cations $\text{Ni}_x\text{Co}_{1-x}\text{Se}_2$. According to Vegard's law, and considering a linear approximation, the amount of Co present in the structure is estimated at $x=0.46$ for the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ sample. The composition deviation obtained from Vegard's law can be attributed to the different bonding forces of Ni and Co with selenium within the selenide.³³ As can be seen in the EELS compositional maps (Figure 5.4c), the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ NPs display a homogeneous distribution of the three elements, with an average ratio $\text{Ni}/\text{Co}=7/3$, consistent with the nominal composition and EDS data. The adsorption–desorption isotherms obtained from the as-prepared NiSe_2 and $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ NPs are displayed in Figure 5.5. BET specific surface areas of 6.2 and 6.9 $\text{m}^2 \text{g}^{-1}$ were calculated for NiSe and $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ NPs, respectively. Besides, the average pore diameter obtained by the BJH model was 45.4 and 51.3 Å for NiSe and $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ NPs, respectively (Figure 5.5b, d).

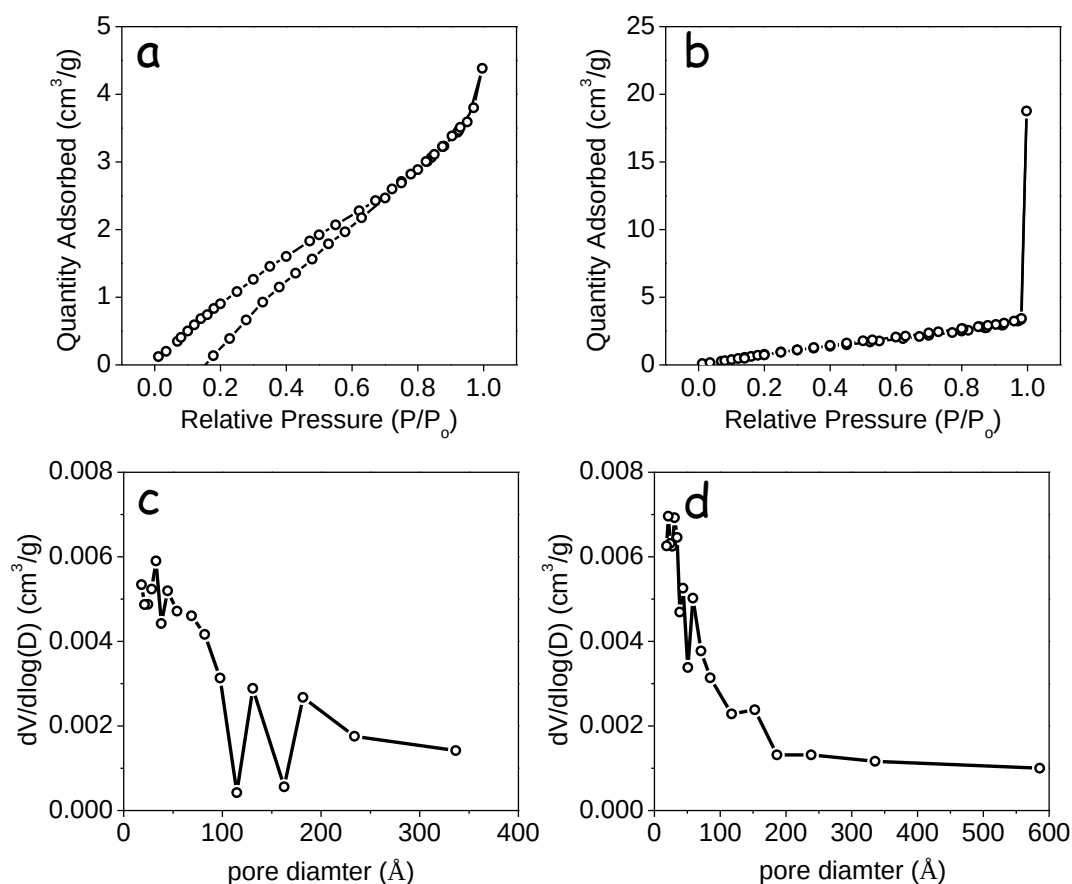


Figure 5.5. Adsorption-desorption isotherm obtained from NiSe₂ (a) and Ni_{0.75}Co_{0.25}Se₂ (b) NPs, and the corresponding pore size distribution for NiSe₂ (c) and Ni_{0.75}Co_{0.25}Se₂ (d) using BJH model.

XPS analysis was used to characterize the surface composition and element oxidation state (Figure 5.4d). Figure 5.4d displays the high resolution Ni 2p_{3/2}, Co 2p_{3/2}, and Se 3d XPS spectra of Ni_{0.75}Co_{0.25}Se₂ NPs. Each of the three elements presents two chemical states that we associate with a metal selenide and a metal oxide environment, in good agreement with previous publications including an XPS characterization of nickel- and cobalt- selenides.^{34,35} Specifically, aside from a satellite peak at 859.8 eV, the Ni 2p_{3/2} region shows the presence of two chemical states that we associate with Ni ions within Ni-Se (852.6 eV) and within Ni-O (854.7 eV) chemical environments.³⁶ The Co 2p_{3/2} region also shows two chemical environments associated with Co-Se (778.0 eV) and Co-O (779.4 eV).³⁷ Finally, the Se 3d XPS spectrum shows a component at 53.4 eV associated with a metal selenide environment and a component at 58.4 eV associated with a selenium oxide environment.³⁸ The surface oxide component was attributed to the partial oxidation of the NPs surface during XPS sample preparation and transportation.³⁹

Table S1. Summary of electrochemical parameters of the Ni_{1-x}Co_xSe₂ NPs in an alkaline system with or without ethanol.

Ni _{1-x} Co _x Se ₂ <i>x</i>	ECSA (cm ² g ⁻¹)	1 M KOH			1 M Ethanol	
		E _{pa} (V)	E _{pc} (V)	Δ E _p (mV)	E _i [*] (V)	E _i [*] (V)
0	75.7	1.381	1.219	162	1.698	1.397
0.25	90.1	1.328	1.249	79	1.672	1.339
0.50	71.0	1.275	1.235	40	1.638	1.379
0.75	49.7	1.209	1.189	20	1.620	1.389
1	-	-	-	-	1.599	1.509

Note: E_i^{*} was the potential that can generate a current density of 10 mA cm⁻² in the 1 M KOH with or without 1 M Ethanol.

Table S3. IC data from solutions obtained after operating the Ni_{0.75}Co_{0.25}Se₂-based electrode at the 2,000th, 4,000th, 6,000th, 8,000th, and 1,0000th s, corresponding to the accomplishment of CA at 1.3, 1.4, 1.5, 1.6, and 1.7 V respectively.

Potentials vs.RHE	Total charge (C)		C _{acetate} (mmol/L)	n _{acetate} (umol)	Q1/Q2 (%)	FE(%)
	Q1	Q2				
1.3	0.016	0.436	0.0	0.0	3.7%	0.0%
1.4	0.030	6.861	0.3	9.2	0.4%	51.9%
1.5	0.123	12.199	1.1	24.2	1.0%	76.6%
1.6	0.941	12.883	2.0	27.7	7.3%	83.0%
1.7	2.389	13.395	2.8	21.4	17.8%	61.7%

Note: Q1 is the total charge passed in 1.0 M KOH solution, collected from Fig. S6a.

Q2 is the total charge passed in 1.0 M KOH solution with 1.0 M ethanol, collected from Fig. 5a.

C_{acetate} is the acetate concentration determined by IC at the 2000th, 4000th, 6000th, 8000th, and 10000th s, corresponding to the accomplishment of CA at 1.3, 1.4, 1.5, 1.6, and 1.7 V respectively.

n_{acetate} is the amount of the acetate produced at 1.3, 1.4, 1.5, 1.6, and 1.7 V within 2000 s CA operation in 1.0 M KOH solution with 1.0 M ethanol.

FE is the faradaic efficiency where determined in 1.0 M KOH solution with 1.0 M ethanol, as displayed in Fig. 5a.

Table S4. IC data from solutions obtained after operating the Ni_{1-x}Co_xSe₂-based electrode at 1.5 V after 10,000 s CA operation in 1.0 M KOH solution with 1.0 M ethanol.

Ni _{1-x} Co _x Se ₂ <i>x</i>	Total charge (C)		C _{acetate} (mmol/L)	n _{acetate} (umol)	Q1/Q2 (%)	FE(%)
	Q1	Q2				

0	0.660	33.909	2.5	8.0	1.9%	91.3%
0.25	1.562	85.607	5.7	18.2	1.8%	82.2%
0.5	1.258	11.678	0.6	2.0	10.8%	64.9%
0.75	1.420	6.764	0.3	1.0	21.0%	57.0%
1	1.871	7.498	0.3	1.0	25.0%	50.8%

Note: Q1 is the total charge passed in 1.0 M KOH solution, collected from Fig. S6b.

Q2 is the total charge passed in 1.0 M KOH solution with 1.0 M ethanol, collected from Fig. 5d.

C_{acetate} is the acetate concentration determined by IC for each sample after 10,000 s CA at 1.5 V.

n_{acetate} is the amount of the acetate produced at 1.5 V after 10,000 s CA operation in 1.0 M KOH solution with 1.0 M ethanol.

FE is the faradaic efficiency where determined in 1.0 M KOH solution with 1.0 M ethanol, as displayed in Figure 5.13.

Working electrodes were prepared by coating a glassy carbon with a catalyst ink prepared by mixing dried NPs and CB in an ethanol/water solution containing Nafion. The electrochemical performance was explored in a conventional three-electrode electrochemical cell using a Pt wire as the counter electrode and a Hg/HgO reference electrode (see the experimental section for details).

First, NiSe₂- and CoSe₂-based electrodes were tested in the potential window 0.9-1.7 V vs. RHE with a scan rate of 50 mV s⁻¹ in 1 M KOH electrolyte solution. In a basic solution, a hydroxide is formed on the surface of Ni oxides and Ni chalcogenides.⁴⁰ As shown in Figure 3a, during the forward scan, the first current density peak measured from NiSe₂-based electrodes (black curve) was attributed to the oxidation of surface Ni(OH)₂ to NiOOH at around 1.392 V vs. RHE. At higher applied potential, above ca. 1.65 V vs RHE, a rise in the current density was associated with the OER. During the reverse scan, NiSe₂-based electrodes displayed a NiOOH to Ni(OH)₂ reduction peak at around 1.380 V vs. RHE.

For the CoSe₂-based electrode in 1M KOH solution (black curve in Figure 5.6b), two small current density peaks in the forward scan were observed. In an alkaline medium, the surface of Co-based chalcogenides is generally oxidized.^{24,41,42} During the forward scan, the surface cobalt oxide is further oxidized probably to CoOOH at 1.11 V vs. RHE. At ca. 1.439 V vs RHE, CoOOH is even further oxidized, possibly to CoO₂. These phases

are reduced during the reverse scan. At ca. 1.60 V vs. RHE, the OER is activated on the CoSe₂-based electrode, showing a significantly higher OER activity than the NiSe₂-based electrode. Upon adding 1M ethanol to the electrolyte solution, a sharp rise in the current density (red curves in Figure 5.6) and corresponding to the ethanol oxidation reaction (EOR) was measured at ca. 1.35 V for both NiSe₂- and CoSe₂-based electrodes. Above the OER onset potential, both reactions, OER and EOR, compete with each other^{43–45}.

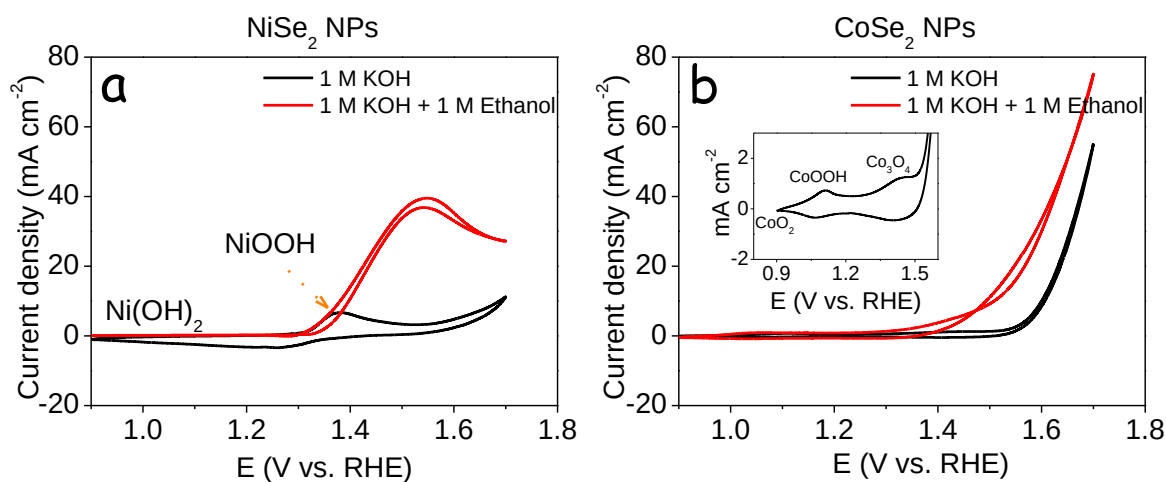


Figure 5.6. CV curves of (a) NiSe₂ NP-based electrodes, and (b) CoSe₂ NP-based electrodes within an electrolyte containing a 1 M KOH (black curve) and a 1 M KOH + 1 M ethanol (red curve).

Figure 5.8 displays the results from the electrochemical characterization of the electrodes based on ternary chalcogenides, Ni_{1-x}Co_xSe₂. In a 1 M KOH solution, we observed the OER activity to increase with the amount of Co. Specifically, as shown in Figure 5.8a, the potential required to generate 10 mA cm⁻² decreased from 1.698 V for NiSe₂, to 1.672 V for x=0.25, 1.638 V for x=0.50, and 1.620 V for x=0.75. These values were still above that of CoSe₂ electrodes, 1.599 V (Table S1).

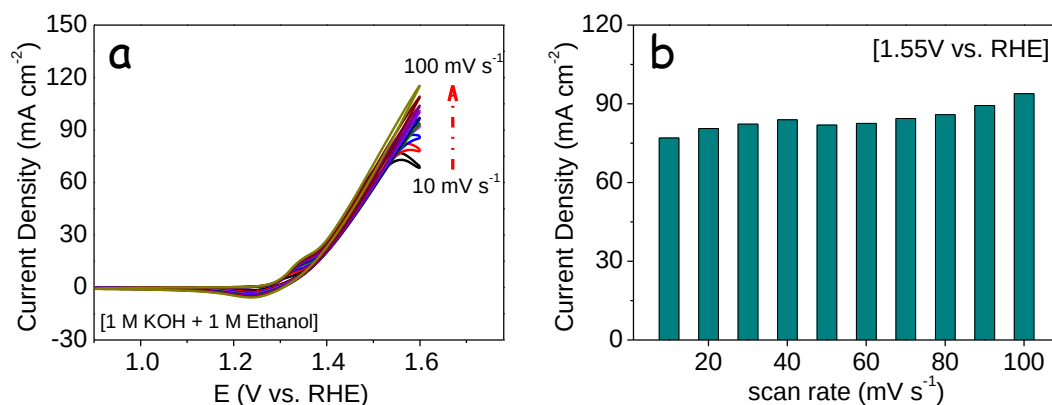


Figure 5.7. (a) CVs curve for the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ in 1 M KOH and 1 M ethanol in the potential window 0.9-1.6 V at a scan rate of 10-100 mV s^{-1} . (b) The current density obtained at 1.55V at a scan rate of 10-100 mV s^{-1} .

When adding 1M ethanol to the electrolyte, a rapid current density increase at lower potentials was observed. In contrast with the OER, the overpotential for EOR at 10 mA cm^{-2} did not follow a monotonous trend with the Co introduction, but we observed the addition of a small amount of Co to result in the highest improvement of the results obtained for NiSe_2 (Figure 5.8b and Table S1). Figure 5.8c compares the current density of the different electrodes at a fixed potential, 1.55 V, significantly below the OER onset potential. After subtracting the current density measured in 1 M KOH solution, the net EOR current density increased from 33.3 mA cm^{-2} for NiSe_2 , to 81.6 mA cm^{-2} for $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$, and decreased at higher Co concentrations. Changing the scan rate in the range 10-100 mV s^{-1} , similar CV curves were obtained for $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ -based electrode in the solution containing 1 M KOH and 1 M ethanol, with a nearly unchanged current density at 1.55 V (Figure 5.7). If considering the loading mass of NPs, the highest mass current density at 1.55 V was also obtained for the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ electrode, 2.1 A mg^{-1} , and it was significantly above that of recently reported Ni NPs/C,⁴⁶ Co_3O_4 nanosheets,⁴⁷ CoNi hydroxide nanosheets,⁴⁸ and fluorine-modified FeOOH ,⁴⁹ and comparable to that of phosphine doped CoS_2 ,⁵⁰ Ni-Fe phosphide and Co_3S_4 nanosheets (Table S2).^{26,51}

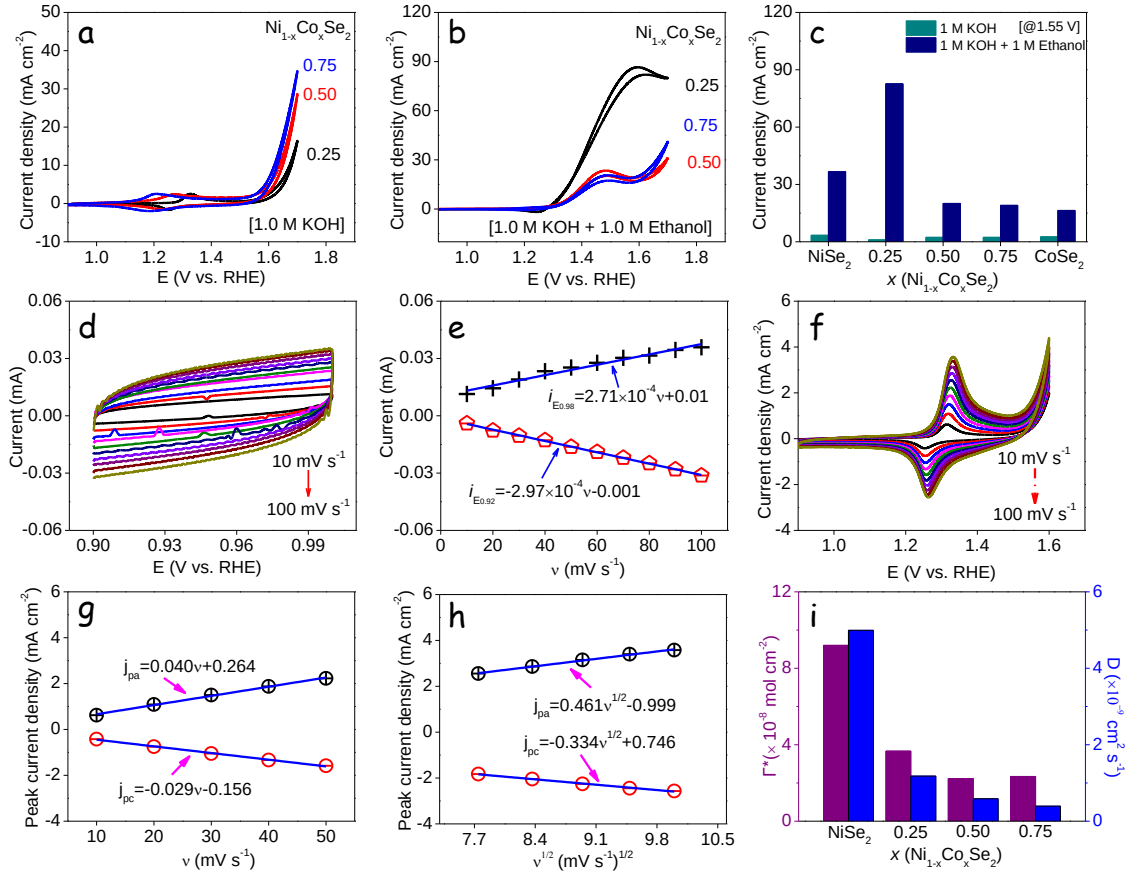


Figure 5.8. (a) CV curves for the $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$ ($x=0.25$; 0.50 ; 0.75) electrodes in 1 M KOH electrolyte in the potential range from 0.9 V to 1.7 V with a scan rate of 50 mV s^{-1} . (b) CV curves in 1M KOH + 1M ethanol electrolyte. (c) Current densities in 1 M KOH (green) and 1M KOH + 1M ethanol electrolyte (blue) at 1.55 V vs. RHE. (d) CV curves of $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$ ($x=0.25$) based electrode in 1.0 M KOH in the non-Faradaic potential range (0.9-1.0 V) with a scan rate of 10-100 mV s^{-1} . (e) Linear fit of the forward current at 0.98 V and backward current at 0.92 V as a function of scan rate, from 10 to 100 mV s^{-1} . (f) CV curves of a $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$ ($x=0.25$) electrode in the potential range from 1.0 V to 1.60 V with a variable scan rate, from 10-100 mV s^{-1} . (g) Linear fit of the peak current and scan rate from 10 to 50 mV s^{-1} . (h) Linear fit of the peak current and square root of scan rate 60 to 100 mV s^{-1} . (i) Comparison of the surface coverage of redox species (Γ^*) and diffusion coefficient (D) for the Ni-containing $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$ NPs based electrode in 1 M KOH solution.

As shown in Figure 5.8d, a double-layer pattern for $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ NPs was obtained in 1 M KOH in the potential window of 0.9 V-1.0 V from 10 mV s^{-1} to 100 mV s^{-1} . The electrochemical double-layer capacitance (C_{dl}) in the non-faradaic region was calculated from the linear fit of the current (i) with the scan rate (v):

$$i_c = v C_{dl}$$

From this capacitance, the electrochemical active area (ECSA) was determined using the following equation:

$$ECSA = C_{dl}/C_s$$

where C_s is 0.04 mF cm^{-2} , according to the values reported for Ni-based electrodes in alkaline solution.⁵² By averaging the slope obtained from the forward scan at 0.98 V and backward scan at 0.92 V (Figure 5.8e), the calculated ECSA for $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ was $90.1 \text{ cm}^2 \text{ g}^{-1}$, well above the values obtained for NiSe_2 ($75.7 \text{ cm}^2 \text{ g}^{-1}$), $\text{Ni}_{0.50}\text{Co}_{0.50}\text{Se}_2$ ($71.0 \text{ cm}^2 \text{ g}^{-1}$), and $\text{Ni}_{0.25}\text{Co}_{0.75}\text{Se}_2$ ($49.7 \text{ cm}^2 \text{ g}^{-1}$) electrodes (Figure 5.9 and Table S1). It should be noted that to determine ECSA, the same value of the specific capacitances was used for all compositions, which is a rough approximation that can account for a part of the ECSA variations observed.⁵³

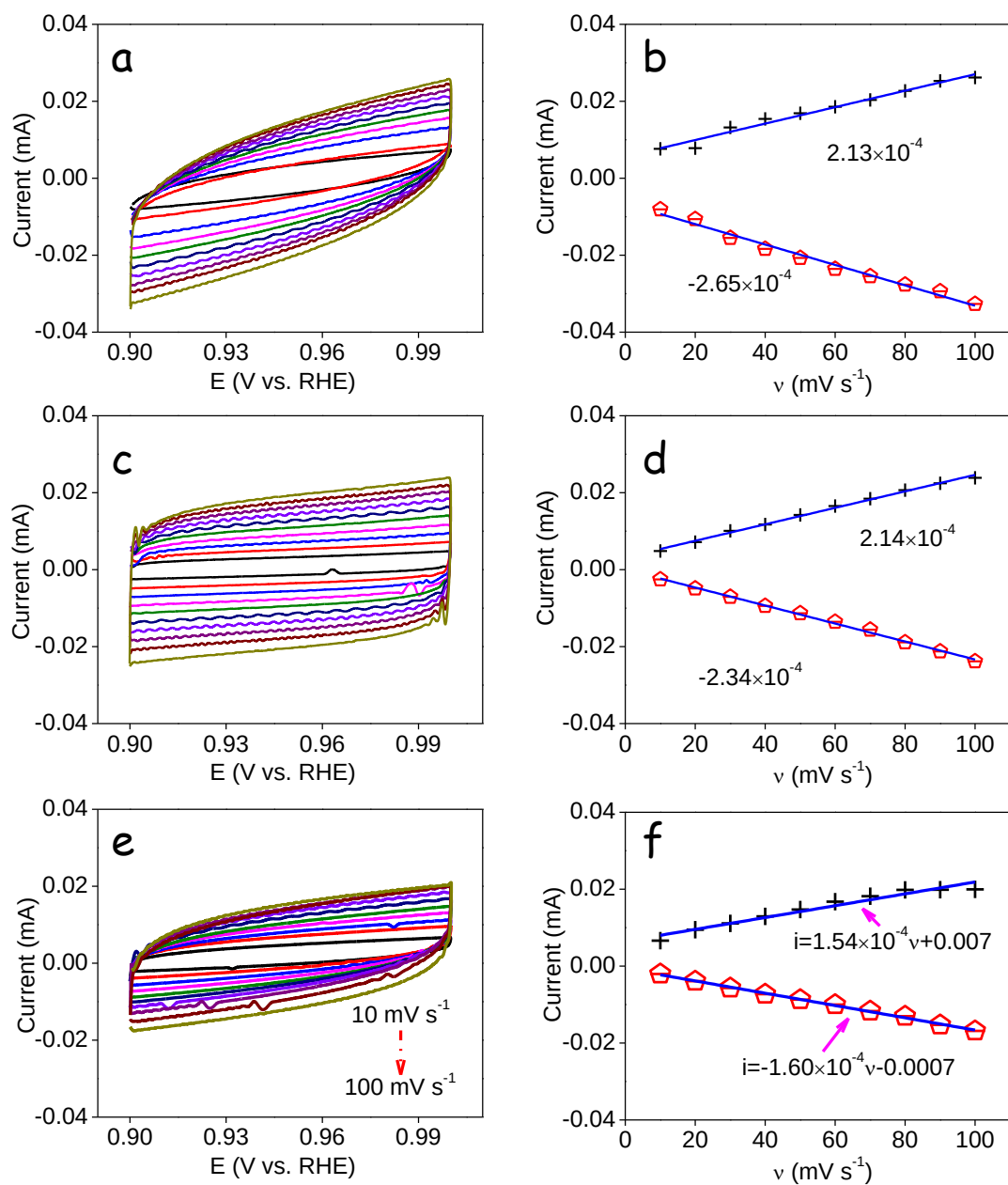


Figure 5.9. CVs curve for the $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$ and linear fitting between the current density and scan rate in the non-faradaic region of 0.9-1.0V (a-b) $x=0$; (c-d) $x=0.50$; (e-f) $x=0.75$;

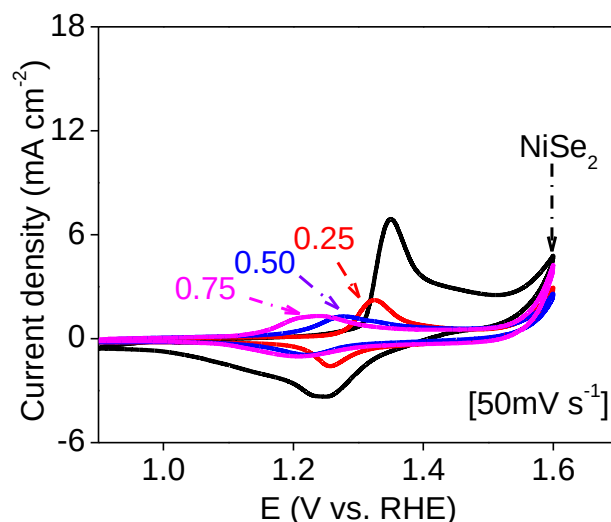


Figure 5.10. CV curves for the $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$ ($x=0; 0.25; 0.50; 0.75$) electrodes in 1 M KOH electrolyte in the potentials range from 0.9 V to 1.6 V with a scan rate of 50 mV s^{-1} .

The CV curves of the bimetallic selenides displayed just one peak in the forward scan and one peak in the reverse scan (Figure 5.10). The peak current density for the bimetallic selenides was found at lower potentials than for NiSe_2 (1.381 V) and the peak potential decreased with the amount of Co introduced, from 1.371 for NiSe_2 to 1.209 V for $\text{Ni}_{0.25}\text{Co}_{0.75}\text{Se}_2$. On the other hand, the voltage of the peak current density in the backward scan did not change monotonically with the amount of Co introduced, but it increased from NiSe_2 (1.219 V) to $\text{Ni}_{0.25}\text{Co}_{0.75}\text{Se}_2$ (1.249 V) and decreased at higher Co concentrations. Associating these peaks to the $\text{Ni}(\text{OH})_2 \leftrightarrow \text{NiOOH}$ redox reaction, we observed the potential difference ΔE_p between the oxidation and reduction peaks decreased from 162 mV for NiSe_2 to 79, 40, and 20 mV with an increasing amount of Co. The smaller potential differences are related to the improved electron transfer kinetics between the electrode surface and the active centres, associated with the modified electronic structure of the bimetallic selenides.⁵⁴

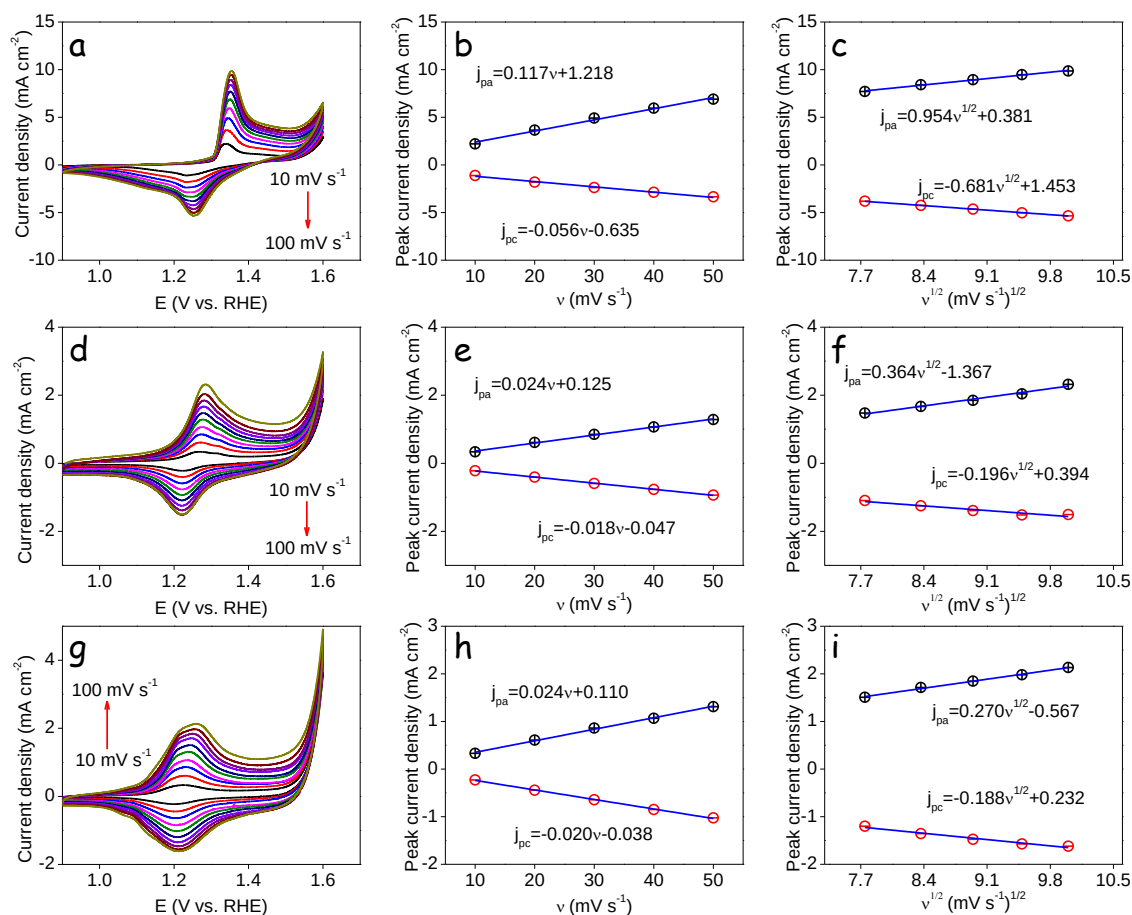


Figure 5.11. CV curves for $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$ electrodes in the Faradaic region of 0.9-1.0V and linear fitting between the peak current density and scan rate and square root of scan rate. (a-c) $x=0$; (d-f) $x=0.50$; (g-i) $x=0.75$;

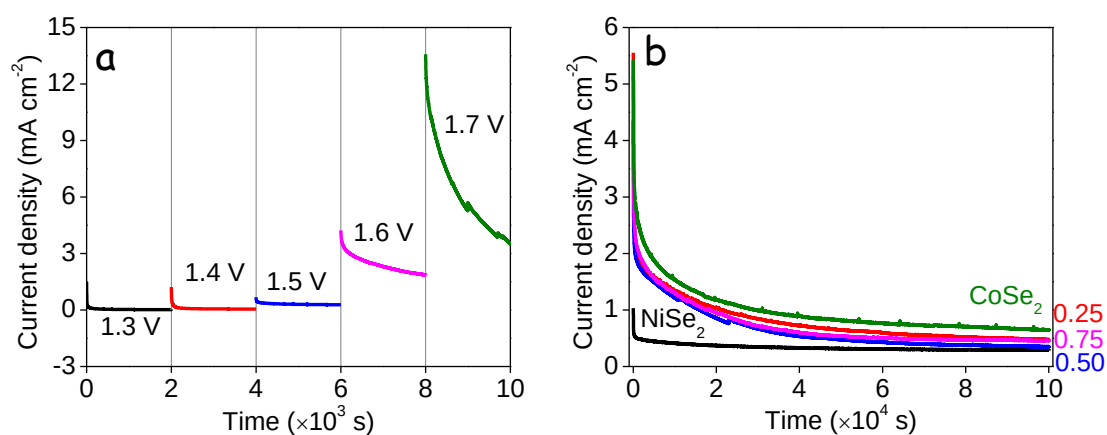


Figure 5.12. (a) CA profile for a $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ electrode at potential from 1.3 V to 1.7 V with 2,000 s operation in 1.0 M KOH. (b) CA profile for $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$ electrode at 1.5 V for 10,000 s testing in 1.0 M KOH.

The surface coverage of Ni(OH)₂/NiOOH redox species was determined from the dependence of the peak current density on the scan rate. Figure 5.8h shows CV profiles from the Ni_{0.75}Co_{0.25}Se₂ electrode in 1 M KOH solution at 10-100 mV s⁻¹. The redox peak associated with the Ni(OH)₂↔NiOOH redox reaction can be observed in the positive and negative scans. From the linear relationship between the peak current density and the scan rate from 10-50 mV s⁻¹, the surface coverage of Ni(OH)₂/NiOOH redox species (I^*) was determined using the following equation:

$$I_p = \left(\frac{n^2 F^2}{4RT} \right) A I^* v$$

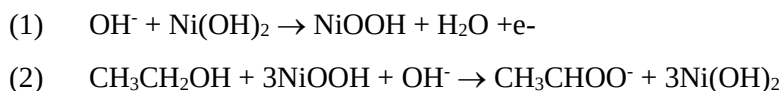
where n is the number of transferred electrons (assumed to be 1 for Ni(OH)₂/NiOOH), F is the Faraday constant (96,845 C mol⁻¹), R is the gas constant (8.314 J K⁻¹ mol⁻¹), T is the absolute temperature (295 K) and A is the geometric surface area of the GC electrode (0.196 cm²). I^* was calculated considering the average of the fitted slopes for the anodic and cathodic peaks. As expected, the surface coverage of redox species, I^* , measured for the Ni_{0.75}Co_{0.25}Se₂ electrode, 3.7×10^{-8} mol cm⁻², was well below that of NiSe₂, 9.2×10^{-8} mol cm⁻², but slightly above the values obtained from materials containing higher amounts of Co (Figure 4i and S8). These values were consistent with those previously obtained from Ni-based chalcogenide.^{55,56}

The proton diffusion is generally regarded as a rate-limiting step that controls the Ni(OH)₂↔NiOOH redox reaction in Ni-based electrodes.⁵⁷ In the scan rate range 60-100 mV s⁻¹ (Figure 4j), both the anodic and cathodic peak current (i_p) were found to be a linear function of the square root of scan rate ($v^{1/2}$), inferring a diffusion-limited redox reaction within the NiSe₂ and the bimetallic selenides. Thus, according to the Randles–Sevcik equation, we investigated the diffusion coefficient (D) of the redox limiting species within the electrodes using the following equation:⁵⁸

$$I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2}$$

where n and C are the electron transfer number (assumed to be 1) and the initial concentration of redox species, respectively. The concentration of Ni(II) was found to be 3.97 g cm⁻³, thus we estimated the C value to be 0.043 mol cm⁻³.^{44,55} Based on this equation, the diffusion coefficient of the redox limiting species in the Ni_{0.75}Co_{0.25}Se₂ electrode was estimated at 1.2×10^{-9} cm² s⁻¹, an order of magnitude above that of the other two Ni-Co-based selenide electrodes (Figure 5.8i and 5.11), but well below that of NiSe₂, 5.0×10^{-9} cm² s⁻¹.

The mechanism of the partial ethanol oxidation to acetate involves two main steps: (1) Ni(OH)₂ activated to NiOOH, and (2) the subsequent oxidation of the adsorbed intermediate.^{59–62}



The $\text{Ni}(\text{OH})_2$ oxidation to NiOOH is generally considered to be the limiting step.⁶³ The partial substitution of Ni by Co within the Ni_2Se certainly implies a slight reduction of the amount of surface NiOOH , but much higher EOR current densities were obtained for $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ when compared with NiSe_2 . This could be directly related to a higher surface area, better kinetics of NiOOH formation, and/or more effective ethanol adsorption by the introduction of Co in the NiSe_2 structure.⁵⁹

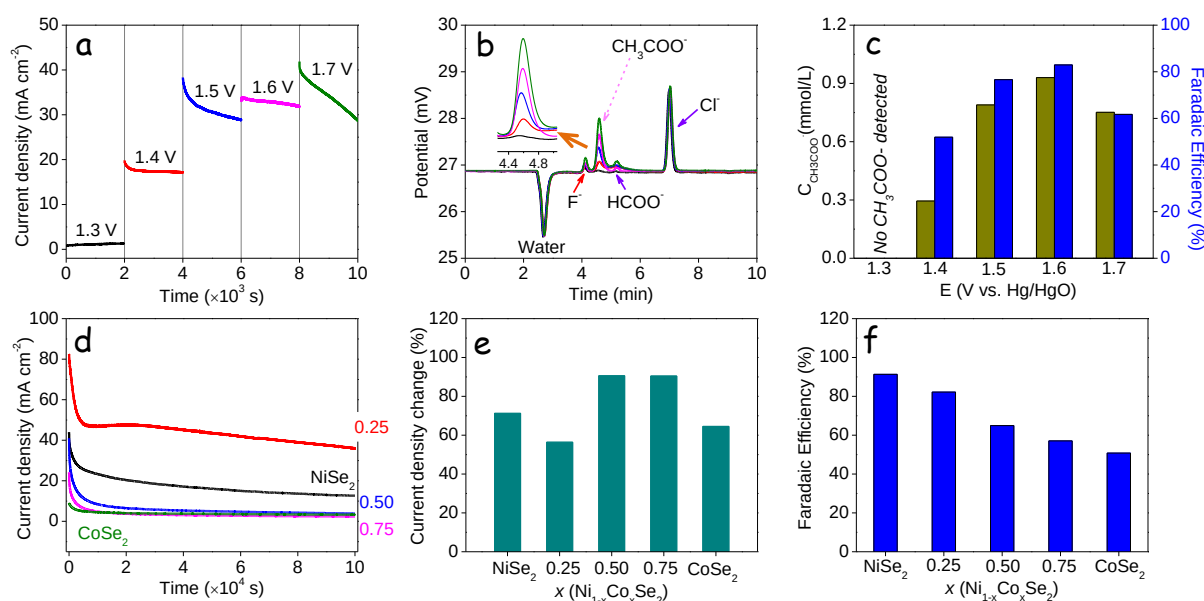


Figure 5.13. Electrochemical performance of the bimetallic selenide electrode in 1M KOH + 1M ethanol. (a) CA curves of continuous 2,000 s operation for $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ NPs at each potential of 1.3, 1.4, 1.5, 1.6, and 1.7 V. (b) IC profile at the end of each 2,000 s intervals. Inset shows the peaks at 4.6 min obtained at each potential. Black, red, blue, pink, and green curves were recorded at the 2000th, 4000th, 6000th, 8000th, and 10000th s respectively. (c) Calculated acetate concentration and Faradaic efficiency after 2,000 s testing at each potential for $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$. (d) CA curves for the selenide over the entire composition range at 1.50 V for 10,000 s testing. (e, f) Corresponding current density change and faradaic efficiency.

Figure 5.13 displays the CA test for $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ electrode in 1 M KOH + 1 M ethanol at 1.3, 1.4, 1.5, 1.6, and 1.7 V. After reacting for 2000 s, a small portion of the electrolyte was analyzed by IC (see details in the experimental section). As shown in Figure 5.13b, the peak at 4.6 min in the IC profile was associated with acetate, which was the only identified product of the ethanol electrooxidation on $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ electrodes. No acetate was detected at 1.3 V, where EOR was not activated on NiOOH . The cumulative acetate concentration in solution was quantified at 0.29, 1.08, 2.01, 2.77 mmol L⁻¹ corresponding to 9.2, 33.5, 61.1, and 82.6 μmol acetate produced at 1.4, 1.5, 1.6, and 1.7 V, respectively. If only considering the acetate production at each potential,

the acetate concentration was found to be 0.29, 0.79, 0.93, and 0.75 mM, equaling to 9.2, 24.2, 27.7, and 21.4 μmol (Figure 5.13c and Table S3). The acetate production increased with the applied potential, up to 1.6 V. Above this voltage, competition with OER decreased the amount of acetate produced (Figure 5.14).

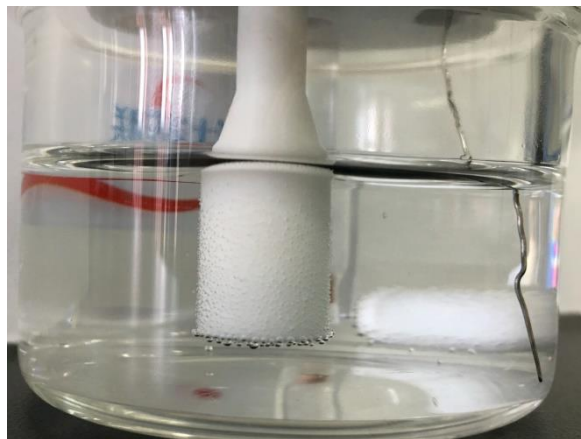


Figure 5.14. Photograph of the electrochemical cell. At a potential of 1.7 V vs. RHE, O_2 bubbles were observed for the CoSe_2 -based electrode after 10,000 s test in 1 M KOH containing 1 M ethanol.

The ethanol-to-acetate Faradaic efficiency (FE) was calculated using the following equation:

$$FE(\%) = \frac{\text{mol of product} \times n \times F}{\text{total charge passed}} \times 100\%$$

where n is the electron transfer number (assumed to be 4 for the ethanol-to-acetate reaction), and F is the Faradaic constant (96485 C mol^{-1}).

For $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ electrodes, the lowest ethanol-to-acetate Faradaic efficiency for the ethanol to acetate was achieved at 1.4 V, and it was found to increase above 80% at 1.6 V, and then decrease at higher potentials due to the activation of the competing OER. More quantitatively, a total charge of 6.9, 12.2, 12.9, and 13.4 C passed through the electrode at 1.4 V, 1.5 V, 1.6 V and 1.7 V, which translated into a Faradaic efficiency of 51.9%, 76.6%, 82.9% and 61.7%, respectively (Table S3). In the absence of 1 M ethanol, the current generated from OER became more obviously at 1.6 V and higher potentials (Figure 5.12a and Table S3).

The long-term stability of the electrocatalyst was tested using CA at 1.5 V. As can be seen in Fig. 5d, almost all the electrodes suffered a rapid decay in current density for the first several minutes. Around 71.3%, 56.4, 90.6%, 90.4, and 64.6% of the initial current densities were lost after 1×10^4 s operation (Figure 5.13e). The activity loss is mainly associated with the accumulation of strongly adsorbed intermediate species poisoning the active surface sites. But changes in the surface chemistry of the electrode, including element rearrangement, surface aggregation of the

elements and phase evolution in alkaline media at a high external potential could also play an important role.^{64–66}

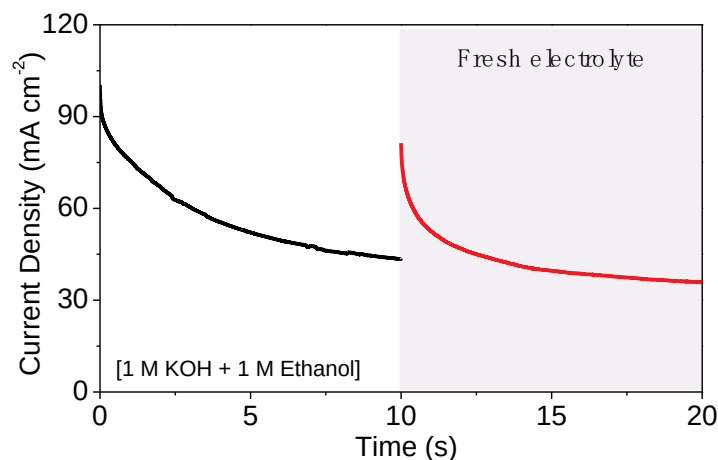


Figure 5.15. Regeneration of the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ NPs-based electrode in 1 M KOH containing 1 M ethanol with two consecutive 10,000s CA operations at 1.5 V by exchanging fresh electrolyte.

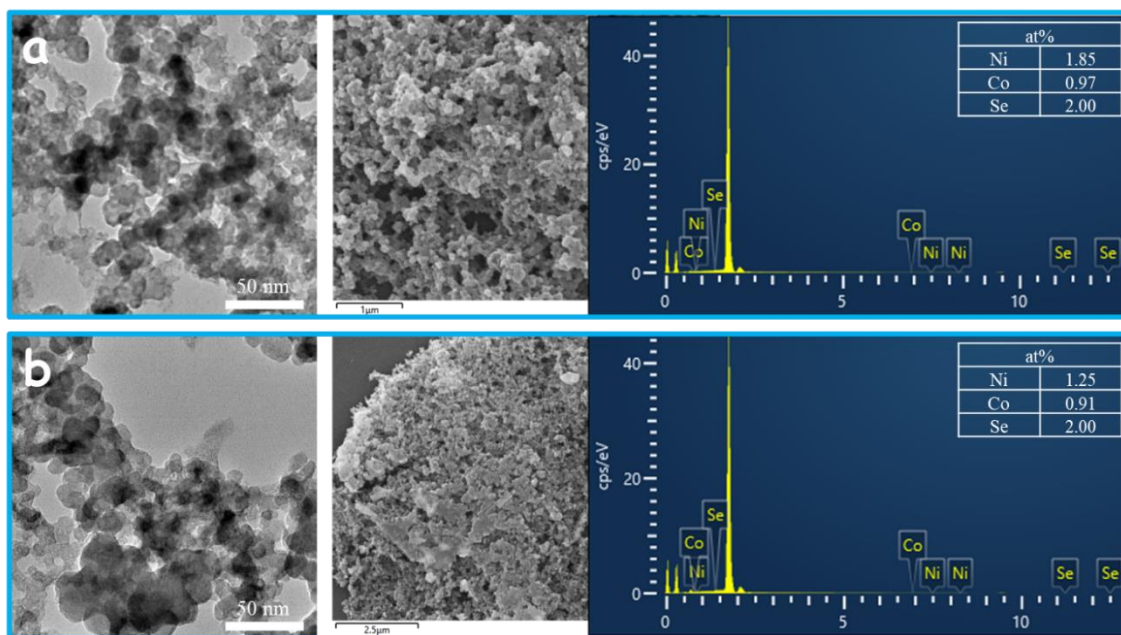


Figure 5.16. TEM and SEM-EDS characterization of the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ -based electrode after 10,000s long-term CA operation of OER (a) and EOR (b) at 1.5 V.

For the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ electrode, a stable current density of 45 mA cm^{-2} , corresponding to 1.2 A g^{-1} , was sustained over the entire test after the initial rapid decay. The current density decay was well below that of other non-precious electrocatalysts as noted in Table S2. Besides, since the regeneration of the electrocatalyst is an important merit for the catalytic process, we run two consecutive CA tests for 10^4 s in 1 M KOH and 1 M ethanol at 1.5 V vs. RHE, replacing the electrolyte in between the two tests. As can be seen in Figure 5.15, similar trends of decay and

significant regeneration behaviours were observed. Specifically, the current density at 1.5 V was largely improved after replacing the electrolyte and the stability was sustained to around 35 mA cm⁻², slightly lower than that obtained during the first CA measurement. As can be seen in Figure 5.16, similar NPs were observed both after long-term EOR and OER CA operation.

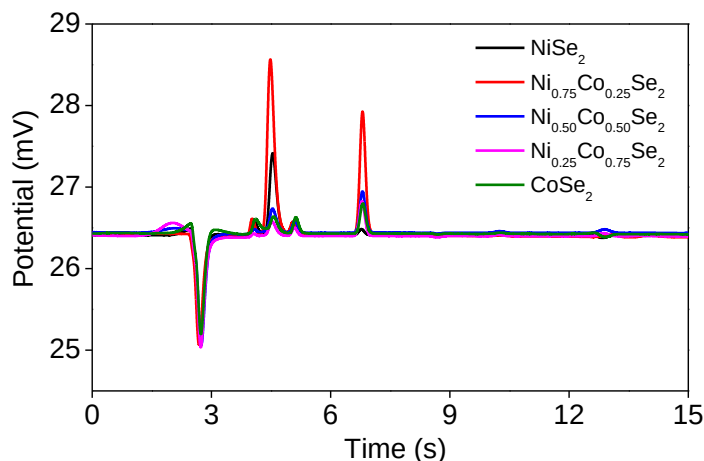


Figure 5.17. IC profile for the electrolyte after long-term CA on Ni_{1-x}Co_xSe₂ electrode in 1.0 M KOH containing 1.0 M ethanol.

IC analysis of the solution after 1x10⁴ s operation (Figure 5.17) showed the produced acetate amount to reach 182.3 μmol for the Ni_{0.75}Co_{0.25}Se₂ electrode, well above the values obtained for NiSe₂ (80.2 μmol) and the other Ni-Co selenides (Table S3). The rate of acetate production on the Ni_{0.75}Co_{0.25}Se₂ electrode was 0.34 mmol cm⁻² h⁻¹. In terms of ethanol-to-acetate Faradaic efficiency, NiSe₂ reached 91.3%, and this value decreased with the incorporation of Co (Table S4).

CA at 1.5 V in 1 M KOH showed the contribution of current not associated to EOR to increase with the Co addition, from 1.9% for NiSe₂ and 1.8% for Ni_{0.75}Co_{0.25}Se₂, to values well above 10% for materials containing higher amounts of Co (Table S4). Thus the decrease of ethanol-to-acetate Faradaic efficiency with the increase of the Co content was associated with the enhanced OER performance.

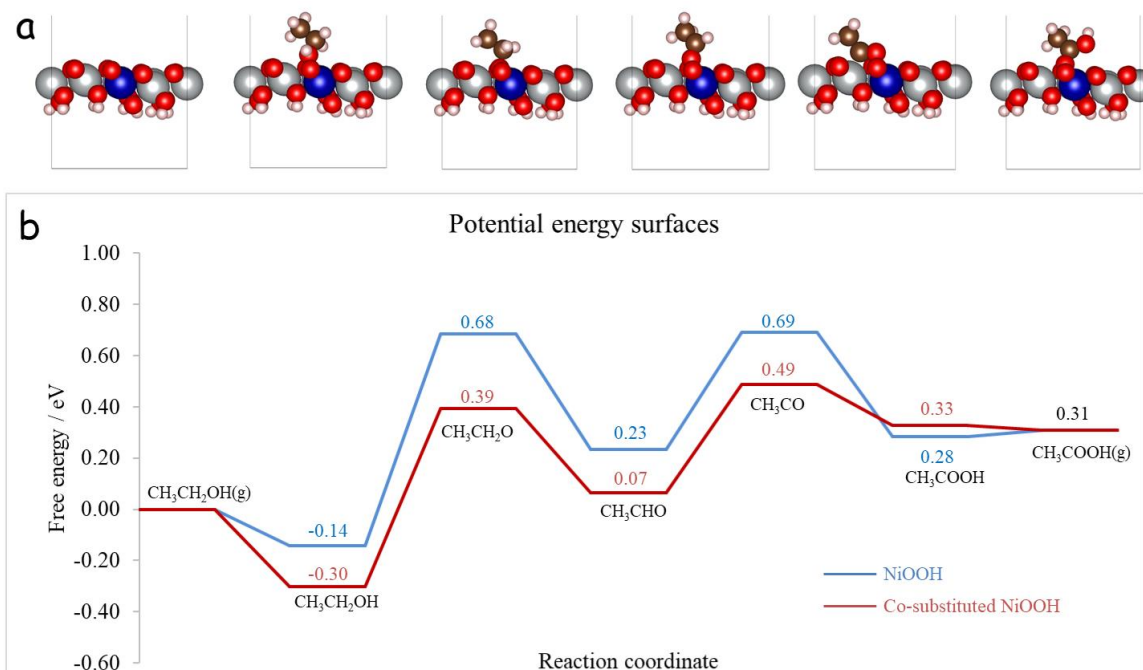


Figure 5.18. (a) DFT optimized adsorbed intermediates on the Co-containing NiOOH surface of $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ electrode, grey ball for Ni, blue for Co, red for O, orange for H, and wine for C. (b) Gibbs free energy diagrams for the ethanol conversion on NiOOH and Co-containing NiOOH surfaces.

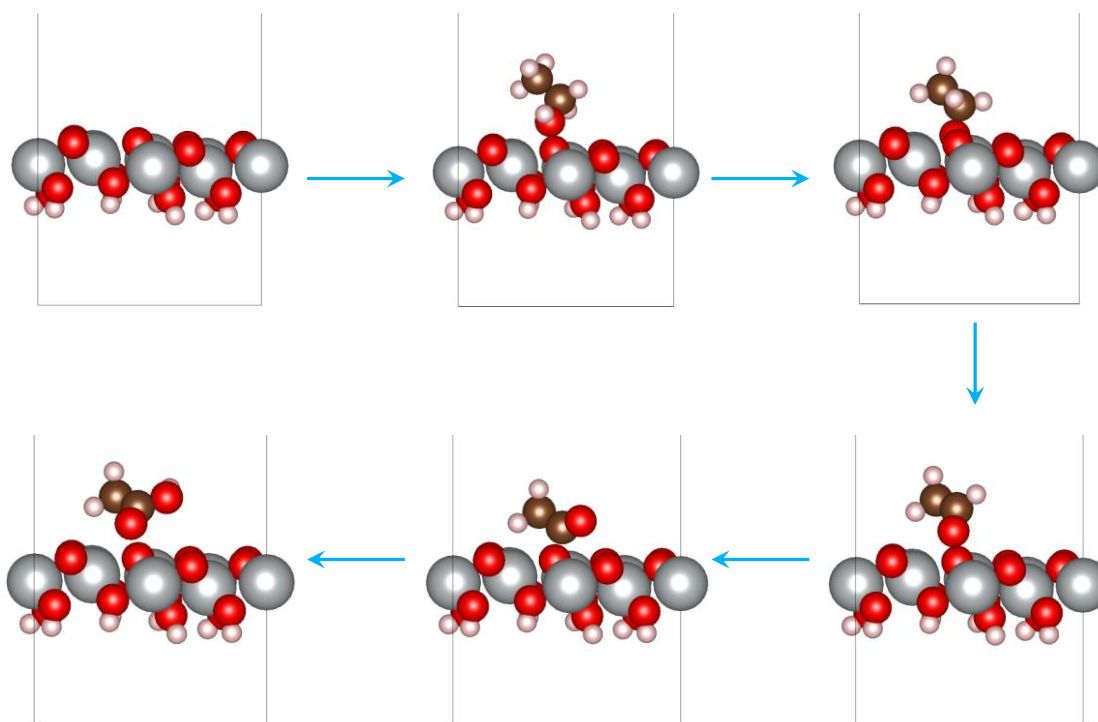


Figure 5.19. DFT optimized adsorbed intermediates on the surfaces of NiOOH surface of NiSe_2 electrode, grey ball for Ni, red for O, orange for H, and wine for C.

The EOR electrocatalytic mechanism and the role of Co in the NiSe_2 electrode were systematically investigated by DFT. Since NiOOH is the active surface for EOR in alkaline

solution, we built two slab models, NiOOH, and Co-substituted NiOOH. Figure 5.18a and 5.19 show the adsorbed intermediates on the NiOOH and Co-substituted NiOOH surface, respectively. Figure 5.18b compares the corresponding Gibbs free energy diagram. The ethanol molecule adsorption energy was calculated to be -0.14 eV and -0.30 eV on the NiOOH and Co-substituted NiOOH surface, indicating stronger ethanol adsorption in the presence of cobalt. The presence of cobalt decreases the formation energy of the intermediate $\text{CH}_3\text{CH}_2\text{O}$ through a dehydrogenation process, from 0.82 eV for NiOOH, to 0.69 eV for Co-substituted NiOOH. The conversion of $\text{CH}_3\text{CH}_2\text{O}$ to CH_3CHO is energetically downwards for both catalysts, with a free energy change of -0.45 eV for and -0.32 eV for Co-substituted NiOOH. Both catalysts show a similar barrier (0.46 eV for NiOOH and 0.42 eV for Co-NiOOH) for the third dehydrogenation step, which results in adsorbed CH_3CO . This dehydrogenation process is generally accompanied by the reduction of NiOOH to $\text{Ni}(\text{OH})_2$. Last, adsorbed CH_3CO is released when interacting with OH^- ions to form CH_3COOH .

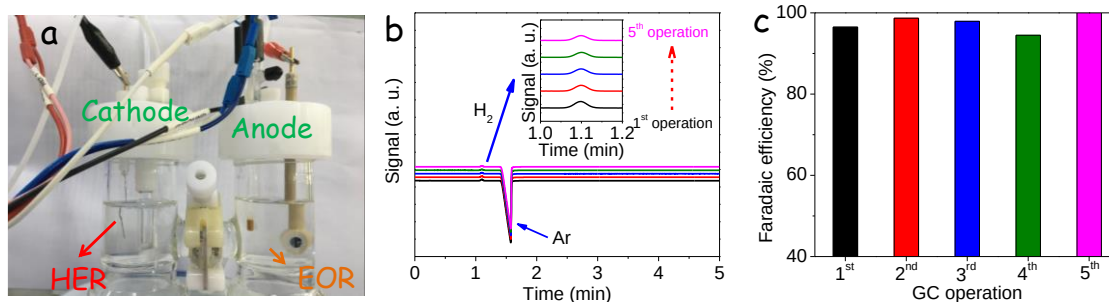


Figure 5.20. (a) Setup for the H-type cell with two compartments. (b) GC curves within 1 hour GC sampling at the cathode. (c) Calculated Faradaic efficiency for HER.

To detect and quantify the gas product generated at the cathode, an H-type cell with two compartments separated by a proton exchange membrane was used (Figure 5.20a). The cell contained 1 M KOH and 1 M ethanol in both compartments. At the cathode side, high-purity Ar was used to carry the produced gas to the GC. As can be seen in Figure 5.20b, two peaks were located at ca. 1.1 and 1.5 min, which were associated with molecular hydrogen and argon. By comparing with known standard hydrogen concentrations, the calculated Faradaic efficiency was determined to be nearly 100% (Figure 5.20c), indicating that only hydrogen was produced on the cathode. In the absence and presence of ethanol in the electrolyte, a total charge of 1.6 C and 85.6 C passed through the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ electrode and the Pt wire, respectively (Table S4). In the presence of ethanol, over 50-fold higher hydrogen was produced during the 10,000 s operation.

5.5 Conclusions

In summary, we developed a solution-based method to produce $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$ NPs with tuned metal ratios. The electrochemical performance of the materials was tested in 1 M KOH and 1 M KOH + 1 M ethanol aqueous electrolytes. CoSe_2 showed enhanced OER activity and NiSe_2 demonstrated a more efficient EOR. The incorporation of small amounts of Co to the NiSe_2 structure resulted in the highest EOR activities. DFT calculations showed that the presence of Co improved ethanol adsorption and decreased the barrier for ethanol dehydrogenation. A current density up to 82.3 mA cm^{-2} was achieved for $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ in 1 M KOH + 1 M ethanol electrolyte at 1.55 V, which is twofold higher than that obtained for NiSe_2 . Over 10,000s testing, the optimized electrocatalyst delivered an average acetate production rate of $0.34 \text{ mmol cm}^{-2} \text{ h}^{-1}$. Additionally, the ethanol-to-acetate faradaic efficiency was determined as 82.3%. This work provides a cost-effective approach to the high Faradaic efficiency electrochemical reforming of ethanol with acetate co-production. This work is also an excellent example for other small molecules oxidation and conversion into valuable chemicals.

5.6 References

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Discussion of Results

The use of electrochemical energy conversion technologies to store electricity in a chemical form and recover it afterwards on demand is particularly appealing to solve the increasing energy crisis issue because of their advantages in terms of cost, sustainability and safety. Among them, an electrolytic cell can directly convert electrical energy into chemical hydrogen energy. The production of hydrogen by water splitting has the following advantages: firstly, it relies on an interfacial chemical reaction, which can allow energy conversion with high thermodynamic and theoretical efficiency; secondly, it allows storing electricity into chemical energy at any time and location, since water is an abundant resource; finally, and most importantly, the combustion of hydrogen eventually only produces water, which almost no impact on the environment. Besides, the produced water can be electrolyzed to produce hydrogen again, so it is a recyclable and pollution-free energy conversion process. These advantages make it one of the most potential energy technologies in the future.

Direct fuel cells are portable power generation devices that convert chemical energy into electrical energy with high efficiency and environmental friendliness through an electrode-electrolyte system. They are considered to be one of the most promising sustainable energy conversion technologies. Compared with traditional combustion and power generation technologies, and also batteries, fuel cells have many advantages, such as no need for a long charging process, both fuel and oxidant can be supplied from the outside of the device, high energy conversion efficiency, and most importantly, the fuel cell produces only CO_2 and H_2O , could effectively reduce NO_x , SO_2 and particulate matter emissions. Direct alcohol fuel cells that replace fossil fuel with liquid fuels such as methanol and ethanol have attracted more and more attention due to the abundant sources of liquid fuels, easy storage and transportation, and high energy density.

Noble metals are widely used as catalysts in these applications due to their excellent activity. Nevertheless, the rare and expensive feature has limited their direct application in the industry. The advance of these technologies toward high efficiency and performance finds opportunities in cobalt-based nanocatalysts. However, the cobalt-based nanocatalysts for energy conversion are still at the proof-of-concept level. The performance of the alone cobalt catalyst is far from ideal. Some composite cobalt-based

nanocatalysts have been developed by introducing other transition metals such as Mo and Ni in this thesis.

The results section started by presenting a new method to produce highly efficient cobalt-based MoCo_xO_y electrocatalyst for OER based on ion etching and pyrolysis assisted strategy by using ZIF-67 as template. As shown in the thesis, the incorporation of molybdate ions not only modifies the material architecture to generate two-dimensional layered nanosheet structures, but also regulates the local coordination environment and electronic structure of the cobalt oxide. The incorporation of molybdenum introduces abundant vacancies and oxygen adsorbed species. Besides, the amorphous nanosheet architecture of the material favors the presence of surface defects and coordinatively unsaturated sites, boosting the exposure of active sites and further improving catalytic activity. Using several pieces of evidence, I revealed the incorporation of molybdenum to enable a LOM, which is in part responsible for the excellent OER performance obtained. The key contribution of this work presented in the thesis is that the advantage of the ion exchange technology could be taken to produce two-dimensional high-performed OER catalysts, as shown in this work that the polyhedral ZIF-67 would be transformed into ultrathin nanosheet demonstrated much better performance comparing to other catalysts. The enhanced activity was mainly ascribed to the much larger surface area, abundant defect sites. Based on this work, other two-dimensional nanomaterials can be synthesized by similar methods.

Next, I analyze the effect of anions on such Co oxide-based electrocatalysts, and particularly $\text{CoFe}_x\text{O}_y\text{-SO}_4$. Some studies have shown that transition metal phosphides and chalcogenides are not really catalysts, but only pre-catalysts. They are transformed into hydroxides and oxyhydroxides during the OER process. However, the role of anionic groups from nonmetal elements is often overlooked. Cobalt-iron oxide nanosheets containing SO_4^{2-} anionic groups were produced from the etching and partial cation exchange of cobalt-based ZIF-67 with an ammonium iron sulfate. The salt breaks the polyhedral structure of ZIF-67, yielding porous assemblies of nanosheets, containing controlled amounts of iron and sulfate ions. The material composition and crystal structure can be adjusted to optimize its OER performance. The excellent performance is associated with the presence of the three elements, cobalt, iron and sulfate ions, and to the porous and amorphous structure of the material. In situ Raman spectroscopy analysis

correlated with XPS data probes the material to be further oxidized to an oxohydroxide phase. It is further demonstrated here, that $\text{CoFe}_x\text{O}_y\text{-SO}_4$ samples catalyse the OER through an effective LOM mechanism. This work suggests that with a new strategy, after anion modification, the OER catalyst activity of electrocatalysts will be greatly improved.

Subsequently, I develop a two-dimensional composite cobalt-based nanomaterial obtained by ion exchange, after calcination and phosphating, transforming into cobalt-based phosphide nanosheets. I particularly engineer ultrathin CoMoP nanosheets using the Co-MOF ZIF-67 as a self-sacrificial template and ammonium molybdate as a shape-defining agent and Mo source. CoMoP nanosheets exhibit outstanding performance towards HER and OER in alkaline media, which I associate with the proper transport properties and electronic energy levels provided by their composition and their porous nanosheet structure. This work provides a suitable strategy to synthesize high-performance Co-MoP electrocatalysts with abundant exposed active sites and effective avenues for charge and electrolyte transport, and it can be employed to further tune the structure and composition of other 2D nanostructures with optimized performance towards OWS and other electrocatalytic reactions.

Because the preparation method of the catalyst has a great influence on the performance and cost of the catalyst, which is also the main problem in industrial applications, a molecular ink method was developed to produce $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$ NPs with tuned metal ratios. The binary solvent mixture based on ethanedithiol (Edt) and oleylamine to produce molecular ink put forwarded by the Brutchey group several years ago could be a better option. In the amine-thiol system, the main difficulty to prepare a phase pure material is to find the proper amine and thiol mixture, their ratio and reaction conditions to crystallize the targeted product in the desired phase, preventing the formation of unwanted secondary phases. In this direction, a series of investigations have been done and the results allowed optimizing the ratios amine/thiol and Co/Ni. The obtained CoSe_2 showed enhanced OER activity and NiSe_2 demonstrated a more efficient EOR. The incorporation of small amounts of Co into the NiSe_2 structure resulted in the highest EOR activities. DFT calculations showed that the presence of Co improved ethanol adsorption and decreased the barrier for ethanol dehydrogenation. This work provides a cost-effective approach to the high Faradaic efficiency electrochemical

reforming of ethanol with acetate coproduction. This work is also an excellent example of other small molecules oxidation and conversion into valuable chemicals.

From the discussion above, it could be seen that the results obtained from the four-research works published have a close relation. The cobalt-based catalysts have good OER performance. By introducing a second transition metal, the morphology, composition and performance of the catalysts are greatly changed, which is used for overall water splitting and ethanol oxidation. Based on all the results shown in this thesis, cobalt-based nanocatalysts, with a rational design of synthesis method, could be promising candidates for electrochemical energy conversion.

Conclusions

In this thesis, four cobalt-based nanocatalysts have been rationally developed and their applications in various electrochemical energy conversion processes have been investigated. From these investigations we reached the following conclusions:

1) Amorphous ultrathin MoCo_xO_y nanosheets with excellent OER catalytic performance, were prepared through an ion etching and pyrolysis assisted strategy. The incorporation of molybdate ions not only modifies the material architecture to generate two-dimensional layered nanosheet structures, but also regulates the local coordination environment and electronic structure of the cobalt oxide. The incorporation of molybdenum introduces abundant vacancies and oxygen adsorbed species. Besides, the amorphous nanosheet architecture of the material favors the presence of surface defects and coordinatively unsaturated sites, boosting the exposure of active sites and further improving catalytic activity. Finally, using several pieces of evidence, I revealed the incorporation of molybdenum to enable a LOM, which is in part responsible for the excellent OER performance obtained.

2) Cobalt-Iron oxide nanosheet containing SO_4^{2-} anionic groups were produced from the etching and partial cation exchange of cobalt-based ZIF-67 with an ammonium iron sulfate. The salt breaks the polyhedral structure of ZIF-67 yielding porous assemblies of nanosheets, containing controlled amounts of iron and sulfate ions. The material composition and crystal structure can be adjusted to optimize its OER performance. The excellent performance is associated with the presence of the three elements, cobalt, iron and sulfate ions, and to the porous and amorphous structure of the material. In situ Raman spectroscopy analysis correlated with XPS data probes the material to be further oxidized to an oxohydroxide phase. It is further demonstrated here, that $\text{CoFe}_x\text{O}_y\text{-SO}_4$ samples catalyse the OER through an effective LOM mechanism.

3) Ultrathin CoMoP nanosheets were engineered using the Co-MOF ZIF-67 as a self-sacrificial template and ammonium molybdate as a shape-defining agent and Mo source. CoMoP nanosheets exhibit outstanding performance towards HER and OER in alkaline media, which we associate with the proper transport properties and electronic energy levels provided by their composition and their porous nanosheet structure. This work

provides a suitable strategy to synthesize high-performance Co-Mo-P electrocatalysts with abundant exposed active sites and effective avenues for charge and electrolyte transport, and it can be employed to further tune the structure and composition of other 2D nanostructures with optimized performance towards OWS and other electrocatalytic reactions.

4) A solution-based method was developed to produce $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$ NPs with tuned metal ratios. The electrochemical performance of the materials was tested in 1 M KOH and 1 M KOH + 1 M ethanol aqueous electrolytes. CoSe_2 showed enhanced OER activity and NiSe_2 demonstrated a more efficient EOR. The incorporation of small amounts of Co to the NiSe_2 structure resulted in the highest EOR activities. DFT calculations showed that the presence of Co improved ethanol adsorption and decreased the barrier for ethanol dehydrogenation. This work provides a cost-effective approach to the high Faradaic efficiency electrochemical reforming of ethanol with acetate co-production. This work is also an excellent example for other small molecules oxidation and conversion into valuable chemicals.

Overall, the cobalt-based nanocatalysts are promising to be applied for electrochemical energy conversion. Meanwhile, the in-situ Raman techniques are applied to reveal the reaction mechanism of the electrocatalysis in the catalytic process. In many cases, the elemental cobalt may demonstrate limited/unsatisfied performance, in this direction, reasonable optimizations/treatments could be applied according to the applications undertaken. The composite cobalt-based nanocatalysts could be very useful herein to design high-performance electrocatalysts.

Future works

Though several cobalt-based nanocatalysts were produced and applied in electrochemical energy conversion in this thesis, there are still some problems that need to be solved in energy conversion applications based on the presented results, as well as some challenges in the cobalt-based synthesis and applications that should be further studied. Some of the open questions are the following:

- 1) For the electrochemical reaction in the solution, it is significant to determine the real active sites during/ after the electrocatalytic process, and be aware of the restructuring of electrocatalysts from “pre-catalysts”. Meanwhile, the *in-situ* techniques are necessary to reveal the reaction pathway of electrocatalysis.
- 2) For electrochemical water splitting, the improvement of current density and stability based on cobalt-based nanocatalysts is necessary for the posterior application in the industry. Regarding the synthesis, further investigation on lower cost and faster preparation methods for cobalt-based nanocatalysts should be developed.
- 3) For the EOR, the high cost and easy poisoning during the reaction process need to be solved. In this direction, *in-situ* characterization would be extremely helpful to provide suggestions to further optimize the electrode materials.

Curriculum Vitae

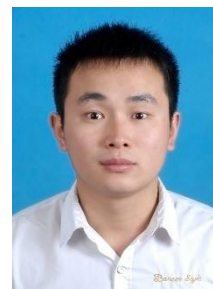
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EDUCATION

2018.11-present, PhD student (Supervisor: Prof. Andreu Cabot)

Universitat de Barcelona, Catalonia Institute for Energy Research, Barcelona, Spain

Major: Nanoscience

Key words: Colloidal synthesis, electrocatalysis (HER, OER, ORR, EOR), Zinc-Air Battery

2015.9-2018.6, Master (Supervisor: Prof. Rong Li)

Major: Chemical Technology

Lanzhou University, School of Chemistry & Chemical Engineering, Lanzhou, China

2011.9-2015.7, Bachelor

Major: Chemical Engineering for Light Industry

Inner Mongolia University of Science and Technology, School of Chemistry & Chemical Engineering, Baotou, China

ACADEMIC RESEARCH EXPERIENCE

2021.4- present, Application of high-entropy alloy nanocatalysts in energy conversion.

2020.6-2021.4, In situ Raman technology for the exploration of the OER reaction mechanism.

2018.11-2020.6, Single-atom catalysts for metal-air batteries.

2015.9-2018.6, Metal-organic framework derived nanomaterials for overall water splitting.

RESEARCH INTERESTS

- Synthesizing colloidal nanoparticles with size, shape and composition control.
- Synthesizing self-supported electrocatalyst for large-scaled catalytic application.
- In-situ characterization, self-rearrangement. Using in-situ techniques to elucidate the transition of electrocatalyst and also the catalytic mechanism by monitoring surface molecules during catalysis process.
- Application: Electrocatalysis; Water splitting, Zinc-Air Battery, Fuel Cell.

PUBLICATION LIST

1. **Wang, X.**; Huang, X.; Gao, W.; Tang, Y.; Jiang, P.; Lan, K.; Yang, R.; Wang, B.; Li, R., Metal-organic framework derived CoTe₂ encapsulated in nitrogen-doped carbon nanotube frameworks: a high-efficiency bifunctional electrocatalyst for overall water splitting. *Journal of Materials Chemistry A* 2018, 6 (8), 3684-3691.

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14. Zuo, Y.; Li, J.; Yu, X.; Du, R.; Zhang, T.; **Wang, X.**; Arbiol, J.; Llorca, J.; Cabot, A., A SnS_2 molecular precursor for conformal nanostructured coatings. *Chemistry of materials* 2020, 32 (5), 2097-2106.
15. Yu, X.; Luo, Z.; Zhang, T.; Tang, P.; Li, J.; **Wang, X.**; Llorca, J.; Arbiol, J.; Liu, J.; Cabot, A., Stability of Pd_3Pb nanocubes during electrocatalytic ethanol oxidation. *Chemistry of Materials* 2020, 32 (5), 2044-2052.
16. Li, J.; Xu, X.; Yu, X.; Han, X.; Zhang, T.; Zuo, Y.; Zhang, C.; Yang, D.; **Wang, X.**; Luo, Z., Monodisperse CoSn and NiSn nanoparticles supported on commercial carbon as anode for lithium-and potassium-ion batteries. *ACS applied materials & interfaces* 2020, 12 (4), 4414-4422.
17. Li, J.; Zuo, Y.; Liu, J.; **Wang, X.**; Yu, X.; Du, R.; Zhang, T.; Infante-Carrió, M. F.; Tang, P.; Arbiol, J., Superior methanol electrooxidation performance of (110)-faceted nickel polyhedral nanocrystals. *Journal of Materials Chemistry A* 2019, 7 (38), 22036-22043.

Annex

Collection of Publications Presented in This Thesis

Cite this: *J. Mater. Chem. A*, 2022, 10, 3659

Activating the lattice oxygen oxidation mechanism in amorphous molybdenum cobalt oxide nanosheets for water oxidation†

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The cost-effective deployment of several key energy technologies, such as water electrolysis, CO₂ electroreduction and metal–air batteries, relies on the design and engineering of cost-effective catalysts able to accelerate the sluggish kinetics of the oxygen evolution reaction (OER). Herein, we detail the synthesis, processing and performance of a cobalt oxide-based OER electrocatalyst with optimized composition, atomic arrangement and nano/microstructure. We demonstrate that doping the cobalt oxide with a higher electronegativity element such as molybdenum promotes the participation of lattice oxygen in the OER. Besides, the processing of the catalyst at moderate temperatures results in an amorphous material with extended compositional and atomic arrangement versatility. Additionally, the catalyst, which is produced through an ion etching assisted strategy using ZIF-67 as a template, displays a highly porous structure in the form of amorphous ultrathin MoCo_xO_y nanosheets that maximize interaction with the media and facilitate the transport of ions through the electrolyte. After optimizing the molybdenum concentration and structural parameters, the best MoCo_xO_y catalysts exhibited a low overpotential of 282 mV at 10 mA cm^{−2} with a reduced Tafel slope of 60.6 mV dec^{−1}, and excellent stability with more than 60 h operation without significant activity decay.

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Introduction

The energy efficiency of several key energy processes and technologies, including water electrolysis, nitrogen and CO₂ reduction, regenerative fuel cells and rechargeable metal–air batteries, is in large part limited by the sluggish kinetics of the oxygen evolution reaction (OER).^{1–4} On top of the moderate efficiencies, current best OER catalysts are based on high cost and rare elements, such as IrO₂ and RuO₂, which further limits the cost-effectiveness of these technologies.⁵ To overcome these

limitations, high activity OER electrocatalysts based on abundant transition metals need to be developed.^{6–8}

In most electrocatalysts, OER proceeds through the adsorbate evolution mechanism (AEM).^{9–11} This conventional mechanism requires catalysts with proper adsorption sites, *i.e.* surface sites that, according to the Sabatier principle, bind reactants/intermediates/products neither too strongly nor too weakly.^{12,13} Recently, several works have evidenced that some OER oxide catalysts are particularly active due to the participation of lattice oxygen in the reaction.^{14–16} In this lattice oxygen oxidation mechanism (LOM), the catalyst performance does not rely on how close to the top of a volcano-like trend their surface adsorption sites lay, but on the covalence of the metal–oxygen bonds and the suitability of the catalyst surface but also bulk electronic structure. These parameters can be tuned by adjusting the catalyst bulk composition, introducing vacancies or extrinsic metal dopants.^{17–20} More specifically, LOM can be particularly promoted through doping with high electronegative cations that facilitate the participation of lattice oxygen in the reaction.²¹

Transition metal oxides (TMOs) have been widely explored as promising electrocatalysts for OER in alkaline medium (4OH[−] → O₂ + 2H₂O + 4e[−]).^{22–25} Within a LOM mechanism, to optimize the OER performance of a catalyst, the oxygen p band needs to be shifted close to the Fermi level to trigger the redox activity of

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the lattice oxygen. This requires strong metal d- and oxygen p-band overlap.²⁶ Cobalt-based oxides and particularly oxohydroxides are particularly interesting owing to their high thermal stability, abundance, suitable 3d electronic configuration, and potential layered structure that allows water penetration to interact with the whole material. The most effective strategy to increase the covalence of the cobalt oxide framework and promote LOM is to lower the energy of the transition metal d orbital by incorporating a more electronegative metal. Thus, an excellent candidate dopant to promote the OER activity of cobalt oxides is molybdenum.

Mo⁶⁺ is a high-valence 4d transition metal ion with a 0.62 Å ionic radius that matches well with that of Co³⁺ (0.63 Å). These similar sizes allow for Mo doping into CoO_x in the form of substituted Co³⁺.^{27–29} Mo doping has been evidenced to improve the electrical conductivity and stability of different host materials.^{30,31} Besides, high valence metal ions and particularly Mo⁶⁺ can induce the targeted downshift of the host metal d-band to penetrate the p-band of adsorbed and lattice oxygen, sharing the ligand holes, making lattice oxygen atoms electrophilic, and thus more prone to participate in water oxidation.^{26,33–35}

In terms of atomic arrangement, amorphous catalysts are particularly advantageous within a LOM mechanism. Amorphous catalysts offer higher flexibility in terms of composition and atomic arrangement, which allows for more facile incorporation of a wide range of extrinsic dopants and concentrations.³⁶ A higher variety of oxidation states of multivalence metals is also possible in amorphous structures, which contain more unsaturated coordination spheres. Amorphous oxides are also generally characterized by less strongly bonded oxygen ions compared with crystalline materials. Besides, the structural and compositional versatility of amorphous catalysis allows them to locally adapt their structure, *i.e.* atomic distribution and valences, under reduction and oxidation conditions/potentials, which also facilitates the participation of lattice oxygen in the reaction.³⁶ Beyond OER, amorphous catalysts frequently outperform crystalline materials in a variety of catalytic reactions and may require less demanding processing in terms of energy and time.³⁷ Besides, amorphous catalysts also contain abundant and varied defects that could provide adsorption/reaction sites for different species and additional activity.^{36–43} Amorphous materials may also contain a higher percentage of atoms exposed to the media and higher porosity, which allows a thorough diffusion of electrolyte to take advantage of the whole electrocatalytic layer. Indeed, amorphous catalysts generally display higher electrochemical surface areas (ECSA) when compared to crystalline materials.^{44,45} Their flexibility also allows an easier surface and volume reconstruction of active sites that translate into a self-healing ability and thus higher stability. As a drawback, the metal dissolution rate of amorphous materials is frequently higher, which reduces their stability, particularly under demanding operating conditions such as high currents. Additionally, the precise analysis of the catalytic mechanisms and their optimization are much more challenging owing to their much higher complexity. Besides optimizing the composition and atomic arrangement, high activity catalysts require a maximized exposure with the media,

and effective transport of electrolyte through the whole catalyst surface. In this direction, the use of ultrathin material architectures such as nanosheets is highly advantageous.^{46–48}

Considering all the above requirements, herein, we detail the synthesis of Mo⁶⁺-doped CoO_x in the form of amorphous and ultrathin sheets from a metal–organic framework (MOF) using an ion etching-assisted strategy. We explore its performance toward OER, comparing it with that of a reference IrO₂ catalyst. The effect of Mo concentration and annealing time on the OER overpotential, Tafel slope and stability is particularly analyzed. Finally, the reaction mechanism is discussed.

Results and discussion

MOFs are crystalline materials with an ordered topological structure that are often used as template for the engineering of porous nanostructured electrocatalysts.^{49–51} We combined this approach with the hydrolysis of an ammonium salt and the simultaneous MOF etching to prepare Mo–Co-based porous materials. A scheme of the synthesis process is displayed in Fig. 1a. As precursor material, we selected a cobalt-based zeolitic imidazolate framework (ZIF-67). First, the template polyhedral ZIF-67 was prepared at room temperature following a reported procedure.^{52,53} Subsequently, Mo–Co MOFs were obtained by ammonium molybdate hydrolysis and simultaneous etching of the ZIF-67. During this process, the hydrolysis of ammonium molybdate generates both protons (H⁺) and hydroxides (OH[−]). H⁺ slowly etch the ZIF-67, releasing Co²⁺ ions. At the same time, OH[−] promotes the precipitation of molybdate, cobalt ions and 2-methylimidazole to form an amorphous and layered material that we refer to as Mo–Co MOF. Finally, the obtained product was annealed at 350 °C for 2 h in air to obtain a Mo-doped cobalt oxide, MoCo_xO_y.

Fig. 1b displays a representative scanning electron microscopy (SEM) image of the ZIF-67 template, which shows a smooth rhombic dodecahedron morphology with a uniform particle size of about 350 nm, and high crystallinity, as observed by powder X-ray diffraction (XRD) analysis (Fig. 2a). As the hydrolysis takes place, Mo–Co MOF nanosheets begin to appear and progressively expand around the ZIF-67 template, which gradually disappears (Fig. S1†). Eventually, after 12 h reaction, the dodecahedron template has fully disappeared and only wrinkled nanosheets are observed (Fig. 1c).

The amount of ammonium molybdate plays a critical role in the morphology of the obtained material. Small amounts of ammonium molybdate (50 mg) do not generate enough protons to entirely consume the ZIF-67 templates, thus resulting in ZIF-67 dodecahedrons with gentle surface wrinkles (Fig. S2b†). This incomplete etching was confirmed by XRD patterns, which displayed the peaks of ZIF-67 in Mo–Co MOFs obtained with 50 mg ammonium molybdate. As the amount of ammonium molybdate increases, the formed Mo–Co MOFs-100 and Mo–Co MOFs-200 gradually become amorphous. On the other hand, when an excess amount of ammonium molybdate is used, some elongated rods, probably MoO₃ coming from the decomposition of the excess of ammonium molybdate, are formed (Fig. S2d and S10†).

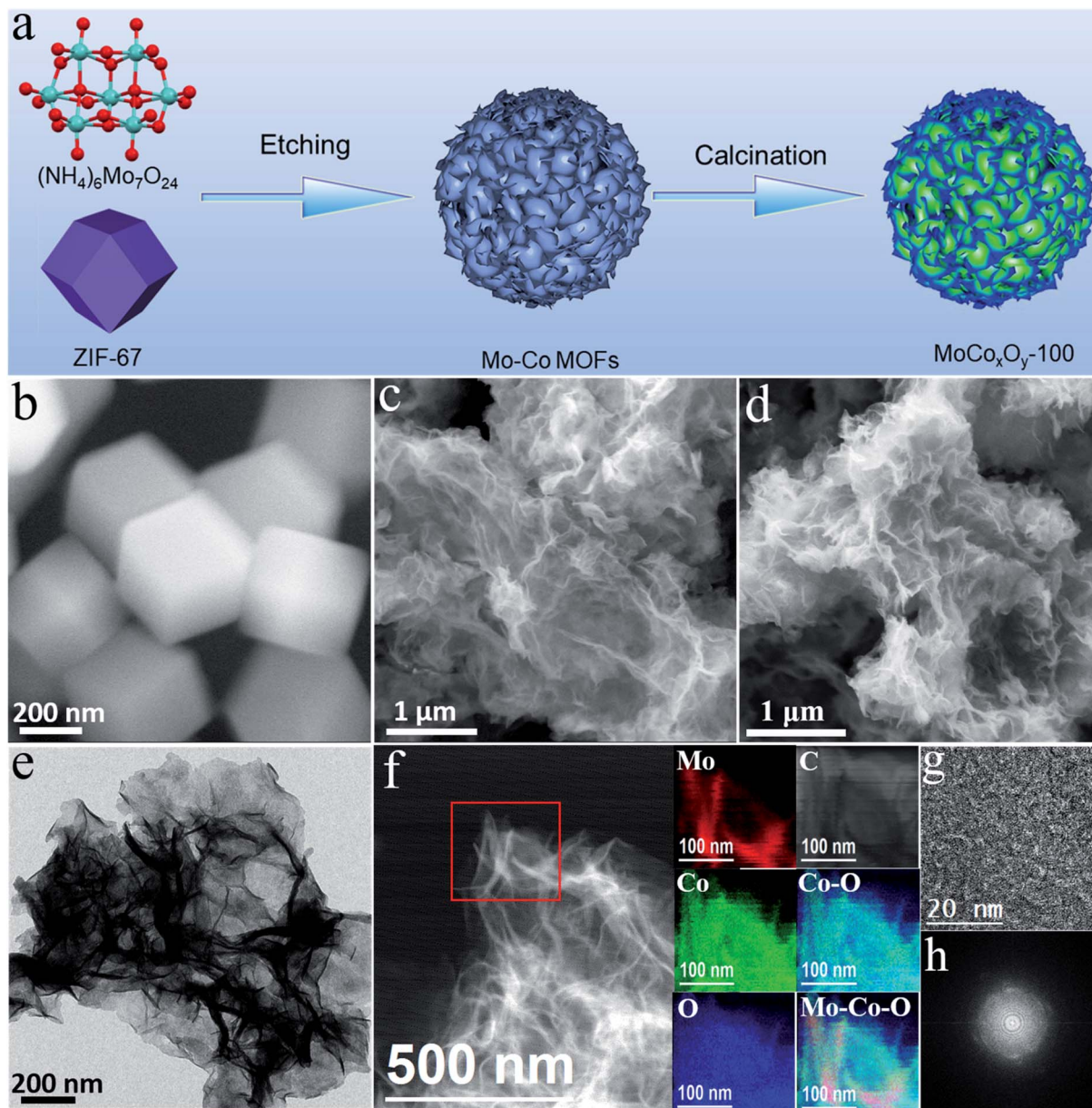


Fig. 1 (a) Scheme of the synthetic route used to produce ultrathin amorphous MoCo_xO_y nanosheets. (b) SEM image of ZIF-67. (c) SEM image of Mo-Co MOF-100. (d) SEM, (e) TEM, (f) HAADF STEM image and EELS chemical composition maps of MoCo_xO_y -100 nanosheets, obtained by using the Mo $M_{4,5}$ -edges at 227 eV (red), Co $L_{2,3}$ -edges at 779 eV (green), O K-edge at 532 eV (blue) and C K-edge at 284 eV (grey) and composites of Co-O and Mo-Co-O. (g) HRTEM image and (h) corresponding FFT spectrum of MoCo_xO_y -100 nanosheets.

Thermogravimetric analysis (TGA) shows weight loss steps at 300 °C and 350 °C for ZIF-67 and Mo-Co MOFs, respectively (Fig. 2c). Thus, we selected 350 °C as the annealing temperature to remove unstable organic ligands but minimizing the loss of carbon, which will aid in promoting the electrical conductivity of the final material. Annealing the material at 350 °C in air did not allow its crystallization, thus the annealed Mo-Co MOFs maintained their amorphous atomic architecture, as observed by XRD (Fig. 2b). After annealing, the nanosheet morphology was also maintained (Fig. 1e and S3†). Atomic force microscopy (AFM) analysis showed the average thickness of the MoCo_xO_y nanosheets to be *ca.* 4 nm (Fig. 2e). Besides, high-resolution

TEM (HRTEM) images and the corresponding indexed fast Fourier transform (FFT) crystallographic analyses confirmed the annealed MoCo_xO_y -100 nanosheets to present no crystallographic ordering. This is in contrast with the good crystallinity of Co_3O_4 nanocrystals obtained by annealing the precursor ZIF-67 at the same temperature (Fig. 2b). Meanwhile, an annular dark-field scanning transmission electron microscope images (HAADF-STEM) and electron energy loss spectroscopy (EELS) mapping showed Mo, Co and O elements to be homogeneously distributed throughout the nanosheets (Fig. 1f and S4†).

Increasing the annealing temperature allowed to partially crystallize the material. Fig. S5c† displays the XRD pattern of

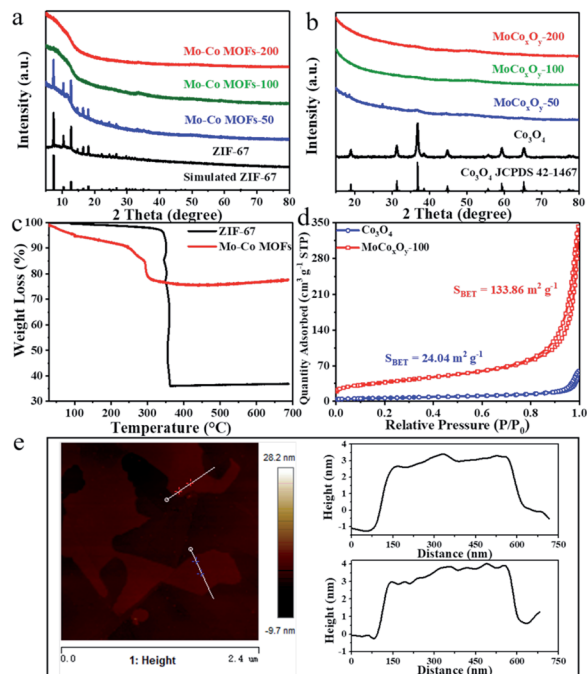


Fig. 2 XRD patterns of (a) the initial MOFs and (b) the annealed MoCo_xO_y samples. (c) TGA curve under air atmosphere of ZIF-67 and Mo-Co MOFs. (d) N_2 adsorption–desorption isotherms for MoCo_xO_y -100. (e) AFM images and the corresponding thickness measurement data of MoCo_xO_y -100.

MoCo_xO_y -100 annealed at higher temperatures, up to 550 °C. Amorphous oxide nanosheets transform into weakly crystalline Co_3O_4 at 450 °C and become a mixture of CoMoO_4 and Co_3O_4 with good crystallinity at 550 °C. Higher temperatures caused the partial collapse of the nanosheet geometry (Fig. S11 and S12†).

The source of molybdenum also has a huge impact on the product morphology. Using sodium molybdate as the molybdenum source, polyhedral ZIF-67 structures were maintained even after 48 h reaction (Fig. S7a†). After annealing this material in air, crystalline Co_3O_4 nanocages were obtained (Fig. S6b, S7b and c†), but EDS analysis showed the amount of molybdenum in these nanocages to be relatively low (Fig. S7d†). MoCo_xO_y displays type-IV nitrogen adsorption–desorption isotherms with an H3-type hysteresis loop at high relative pressures (0.8–1.0 P/P_0 , Fig. 2d). Isotherms provided a Brunauer–Emmett–Teller (BET) specific surface area of 134 $\text{m}^2 \text{g}^{-1}$ for MoCo_xO_y -100 and just 24 for the Co_3O_4 nanoparticles. Besides, the Barrett–Joyner–Halenda (BJH) average pore size and cumulative pore volume were 15.8 nm and 0.53 $\text{cm}^3 \text{g}^{-1}$ for MoCo_xO_y -100, and 17.2 nm and 0.09 $\text{cm}^3 \text{g}^{-1}$ for Co_3O_4 nanoparticles (Fig. S13†). These results indicate that MoCo_xO_y -100 is characterized by a suitable mesoporous structure to provide a high electroactive surface area and at the same time facilitate the transport rate of reactants and reaction products.^{54,55}

Fig. 3a shows the Raman spectra of Co_3O_4 and MoCo_xO_y obtained from the annealing of ZIF-67 and Mo-Co MOF, respectively. Four obvious peaks were observed in the Co_3O_4

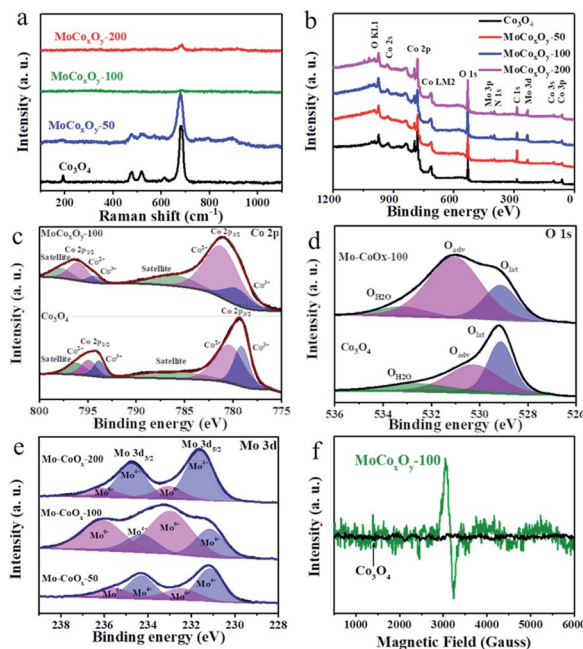


Fig. 3 (a) Raman and (b) survey XPS spectra of Co_3O_4 and MoCo_xO_y samples. (c) Co 2p, (d) O 1s and (e) Mo 3d high-resolution XPS spectra and (f) EPR spectra of Co_3O_4 and MoCo_xO_y -100.

spectrum at 185.5, 465.3, 506.6, and 670 cm^{-1} , which were associated with the F_{2g}^1 , E_g^2 , F_{2g}^2 , and A_g^1 phonon modes of crystalline Co_3O_4 .^{56,57} With the introduction of Mo, the peaks associated with the Co_3O_4 phase gradually disappeared, confirming the amorphous nature of the formed materials. X-ray photoelectron spectroscopy (XPS) analysis showed the presence of elemental C, N, O, Co and Mo in all MoCo_xO_y samples (Fig. 3b), which is consistent with EDS analysis. The high-resolution Co 2p XPS spectra were fitted considering two Co chemical environments, at ca. 779.4 eV ($2p_{3/2}$) and 781.5 eV ($2p_{3/2}$), resembling those of Co within lattice Co_3O_4 and a hydroxide-like environment, respectively (Fig. 3c and S14†).⁵⁸ The lattice Co_3O_4 component was majoritarian in most of the samples, but the hydroxide-like component was dominant in MoCo_xO_y -100. Table S2† displays the ratio of the different surface Co chemical states as determined by XPS analysis.

The asymmetric high-resolution O 1s XPS spectra were fitted with three nearly Gaussian bands (Fig. 3d and S15†). The O_{lat} component, at 529 eV, is attributed to O^{2-} within a metal oxide lattice. The O_{ads} component at 531 eV, is associated with hydroxide ions (OH^-) and/or other chemisorbed and dissociated oxygen species (O^{2-} , O_2^{2-} , or O^-). The area of the O_{ads} XPS band is frequently related to the concentration of oxygen vacancies that are assumed to promote the chemisorption of oxygen-based species. However, it should be noticed that a baseline concentration of chemisorbed oxygen species will be present at most oxide surfaces even in the absence of oxygen vacancies. Finally, the $\text{O}_{\text{H}_2\text{O}}$ component at around 533 eV is usually attributed to adsorbed water.^{24,46,59} As displayed in Table S2†, the relative amount of chemisorbed species is significantly higher in MoCo_xO_y -100 ($\text{O}_{\text{ads}}/\text{O}_{\text{lat}} = 1.48$) than in Co_3O_4 ($\text{O}_{\text{ads}}/$

$O_{\text{lat}} = 0.62$), consistent with the Co 2p XPS spectra. These results indicate the formation of a more extended oxyhydroxide surface layer and/or a higher concentration of adsorbates on samples containing molybdenum, which could be related to a larger concentration of oxygen vacancies.^{60,61} Fig. 3e displays the high-resolution XPS spectra of Mo 3d. The spectra were fitted with two doublets, associated with Mo^{4+} (Mo 3d_{5/2} at 231 eV) and Mo^{6+} (Mo 3d_{5/2} at 233 eV) chemical environments.^{6,28} As displayed in Table S2,[†] the Mo^{4+} component was dominant at the surface of all samples, except for MoCo_xO_y -100 that displayed a higher concentration of Mo^{6+} : $\text{Mo}^{4+}/\text{Mo}^{6+} = 0.76$. The EPR spectra of MoCo_xO_y -100 displays the footprint of oxygen vacancies at $g = 2.12$ (Fig. 3f). This signal was not observed for Co_3O_4 , which points to the key role played by Mo cations in the generation of oxygen vacancies. Notice that the presence of oxygen vacancies have associated the existence of high-energy dangling bonds, which could promote surface chemisorption, as observed from XPS results, and electrocatalytic performances.^{17,32,33,62–64}

The OER electrocatalytic performance of the materials was initially evaluated by linear sweep voltammetry (LSV) in 1.0 M KOH (Fig. 4a). A commercial IrO_2 catalyst was also measured as a reference. Among the tested samples, MoCo_xO_y -100 exhibited the lowest onset potential and the highest current densities. MoCo_xO_y -100 was characterized by an overpotential of 282 mV at a current density of 10 mA cm^{-2} (η^{10}), well below that of IrO_2 (301 mV), Co_3O_4 (350 mV) and Mo-Co MOFs (379 mV). As depicted in Fig. 4b, the Tafel slope of MoCo_xO_y -100 (60.6

mV dec^{-1}) was also well below that of IrO_2 (66.9 mV dec^{-1}), proving the more favourable and faster reaction kinetic of the former.

Comparing materials annealed at different temperatures (Fig. S17a[†]), we observed the catalyst obtained at 350°C to provide the best OER performance. Besides, the molybdenum content also played an important role, with MoCo_xO_y -100 displaying superior performance than MoCo_xO_y -50 and MoCo_xO_y -200 samples (Fig. 4 and S17b[†]). Additionally, we observed the molybdenum source to have a strong influence on the performance of the catalyst, with the material obtained using ammonium molybdate etching displaying a significantly superior performance than the material obtained with sodium molybdate (Fig. S17a[†]).

The outstanding performance of MoCo_xO_y -100 is demonstrated when comparing the η^{10} and Tafel slope of MoCo_xO_y -100 with those of other cobalt-based electrocatalysts (Table S5[†] and Fig. 4c). This outstanding OER performance is attributed to the high density of active sites derived from the amorphous and defective layered nanosheet structure, and potentially to the Mo-activated participation of lattice oxygen in the OER, as discussed below. The charge transfer rate at the catalyst reaction interface was evaluated by electrochemical impedance spectroscopy (EIS).^{6,65} Nyquist plots show the charge transfer resistance (R_{ct}) of MoCo_xO_y -100 to be the smallest among all the tested samples (Fig. 4e), which point at a faster charge transfer rate in this material.

ECSA is the area accessible to the electrolyte ion and it is generally proportional to the electrocatalysts double-layer capacitances (C_{dl}), which was determined from CVs at different scan rates, from 20 mV s^{-1} to 200 mV s^{-1} (Fig. S16[†]). As shown in Fig. 4d, MoCo_xO_y -100 displays the largest C_{dl} value (7.36 mF cm^{-2}), well above that of MoCo_xO_y -50, MoCo_xO_y -200, Co_3O_4 and Mo-Co MOFs. The enhanced C_{dl} indicates that MoCo_xO_y -100 exposes a larger number of active sites. When normalizing to ECSA, significantly higher current densities were still obtained for MoCo_xO_y -100 compared with the other materials, which further demonstrated the higher OER activity of this material, beyond its higher active surface area (Fig. S17b[†]).

Beyond some minor fluctuations associated with the formation of bubbles and temperature oscillations in the laboratory, the chronoamperometric (i - t) durability test showed an almost negligible current change for MoCo_xO_y -100 electrodes after 60 h of operation (Fig. 4f). Meantime, very similar polarization curves were obtained for MoCo_xO_y -100 before and after 2000 cycles, with almost zero attenuation of the cathodic current (Fig. S18a[†]). These results demonstrate the excellent stability toward the OER process of MoCo_xO_y -100.

Within a basic aqueous solution, the surface of Co-based electrocatalysts tends to be oxidized into cobalt oxyhydroxide (CoOOH), which is considered the active OER phase.²⁹ Some previous studies concluded that CoOOH catalysed the OER through a LOM.⁶⁴ In an oxyhydroxide (M-OOH), the LOM involves several steps as simplified in Fig. 5f.^{64,66} Briefly, the first steps involve the interaction with hydroxide ions in solution, the deprotonation of OH^- groups within the oxyhydroxide, and the release of H_2O . Subsequently, O-O bonds are formed within

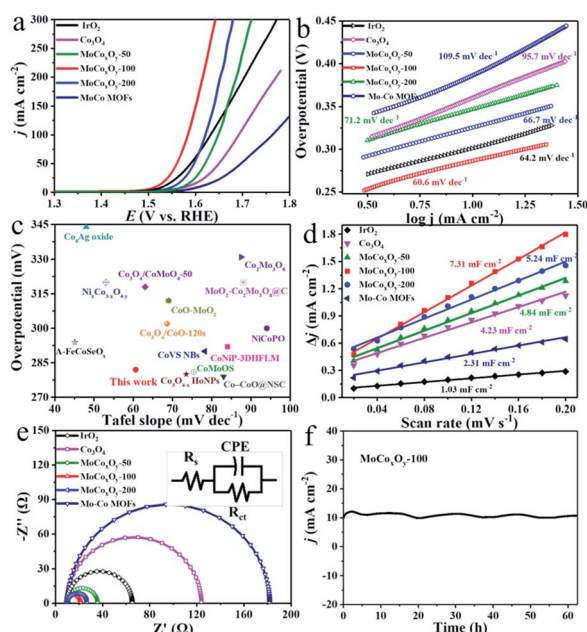


Fig. 4 Electrocatalytic OER performance of the various catalysts. (a) LSV curves. (b) Tafel plots. (c) Comparison of overpotential at 10 mA cm^{-2} and Tafel slopes for MoCo_xO_y -100 and some cobalt-based OER catalysts (Table S5[†]). (d) Capacitive current density measured at 0.95 V vs. RHE plotted as a function of scan rate. (e) Nyquist plots at the potential of 1.55 V vs. RHE. (f) Chronoamperometry curve of MoCo_xO_y -100.

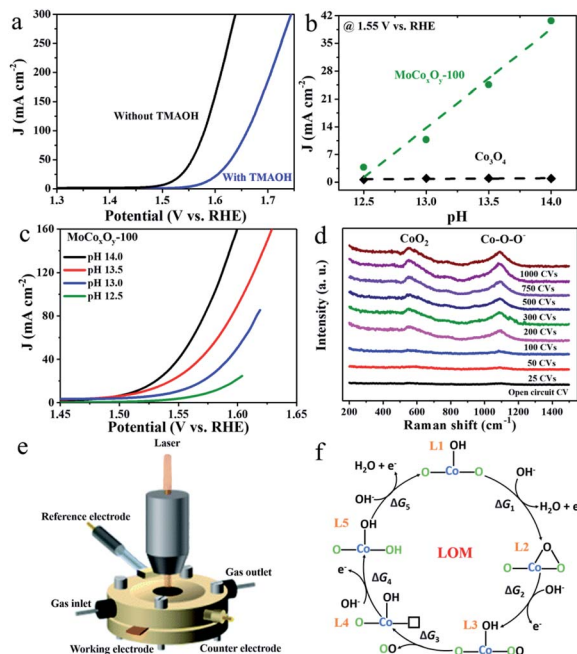


Fig. 5 (a) OER polarization curves of $\text{MoCo}_x\text{O}_y-100$ for pH dependence activities. (b) Current densities $\text{MoCo}_x\text{O}_y-100$ and Co_3O_4 at 1.5 V vs. RHE as a function of the pH value. (c) OER Polarization of $\text{MoCo}_x\text{O}_y-100$ in 1 M KOH without and with TMAOH, respectively. (d) *In situ* Raman spectra of $\text{MoCo}_x\text{O}_y-100$ after different CV cycles in 1.0 M KOH electrolyte. (e) Schemes of *in situ* Raman spectroscopy. (f) Proposed OER reaction mechanism of lattice oxygen participation (LOM), where $\square$ represents an oxygen vacancy.

the oxide structure and O_2 is released. The release of O_2 leaves oxygen vacancies behind, which are filled through the adsorption of additional OH^- , returning the catalyst to its initial state.

A fundamental characteristic of LOM is the direct O–O coupling, which bypasses the need for a correlated intermediate adsorption in the AEM. Thus, to distinguish LOM from AEM one can track the generation of peroxo-like (O_2^{2-}) and superoxo-like (O^{2-}) species. To track the existence of these negatively charged oxygenated species, tetramethylammonium cation (TMA^+) was introduced as a chemical probe into the KOH solution (1 M KOH + 1 M TMAOH). TMA^+ specifically binds with negative oxygenated species, thus hamper the OER *via* LOM. As shown in Fig. 5c, when introducing TMAOH into the KOH solution, the OER activity of $\text{MoCo}_x\text{O}_y-100$ was seriously reduced, which demonstrates the key contribution played by LOM in this material.

Besides, LSV measurements with electrolytes with different KOH concentrations, from 0.032 M (pH 12.5) to 1 M (pH 14.0), were used to investigate the dependence of OER activity on pH (Fig. 5a and b). We observed the $\text{MoCo}_x\text{O}_y-100$ electrocatalyst at 1.55 V vs. RHE to exhibit a strong pH-dependent OER activity on the RHE scale ($25 \text{ mA cm}^{-2} \text{ pH}^{-1}$). In contrast, Co_3O_4 showed a mostly pH-independent OER activity as this same potential ($0.18 \text{ mA}^{-2} \text{ pH}^{-1}$, Fig. S18b[†]). A strong pH-dependent OER activity on the RHE scale is a distinct feature of LOM, associated with its decoupled proton and electron transfer steps.^{33,64,67,68} The observed activity increase can be intuitively understood by

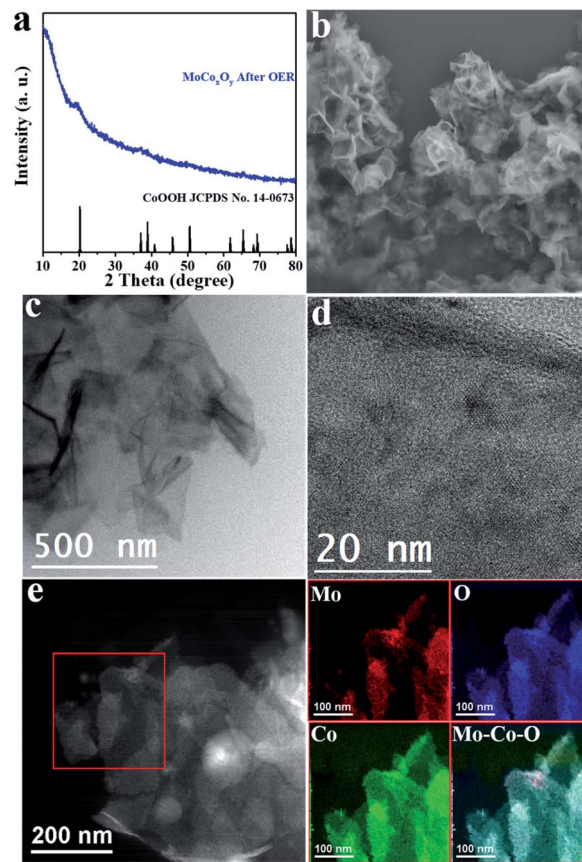


Fig. 6 (a) XRD pattern, (b) SEM general image, (c) TEM, (d) HRTEM, and (e) HAADF STEM image and EELS chemical composition maps of the MoCo_xO_y nanosheets after long time (60 h) durability test.

the easier deprotonation of the OH groups of the oxyhydroxide structure when increasing pH.²¹

Operando Raman spectroscopy was used to gain additional inside of the reaction kinetics in our $\text{MoCo}_x\text{O}_y-100$ catalyst and determine the active species during OER. After 200 CV cycles and above, we observed the appearance of a broad peak at $550\text{--}600 \text{ cm}^{-1}$, corresponding to A_{1g} and E_g vibrational modes of Co–O in CoOOH .^{69,70} Besides, an additional broad band was observed in the $1000\text{--}1200 \text{ cm}^{-1}$ range (peaking at *ca.* 1090 cm^{-1}), which is assigned to a superoxidic specie (CoOO^-).⁶³ The intensity of these bands increased with the CV cycle times, demonstrating the generation and progressive accumulation of these species during the OER process.

The dissolution rate of Mo and Co was monitored by analysing the content of metal in the electrolyte using inductively coupled plasma-mass spectrometry (ICP-MS). As shown in Fig. S19,[†] a negligible amount of Co is dissolved during an 18 h chronoamperometric test at 282 mV vs. RHE. In contrast, a significant amount of Mo was dissolved within the electrolyte during the first 6 h of reaction. The leaching of Mo initially generates metal vacancies within the MoCo_xO_y lattice and posteriorly facilitates the cobalt hydroxide formation.¹⁸ Nevertheless, these transformations have a minor influence on the OER activity according to Fig. 4f and do not modify the

nanosheet morphology of the material that is preserved after long-term OER (Fig. 6). Fig. 6d shows an HRTEM micrograph of the post-OER product displaying obvious lattice fringes. Besides, the XRD pattern of the post-OER material displayed a distinct diffraction peak that was identified with γ -CoOOH (JCPDS 14-0673, Fig. 6a). SEM and TEM images exhibited the ultrathin nanosheet structure to be maintained, without any obvious change after OER cycling (Fig. 6b and c). Moreover, HAADF-STEM images and EELS elemental maps (Fig. 6e) demonstrated a homogeneous distribution of Co, O and Mo within the cycled material.

Conclusions

We detailed the synthesis of amorphous ultrathin MoCo_xO_y nanosheets with excellent OER catalytic performance, through an ion etching and pyrolysis assisted strategy. The incorporation of molybdate ions not only modifies the material architecture to generate two-dimensional layered nanosheet structures, but also regulates the local coordination environment and electronic structure of the cobalt oxide. The incorporation of molybdenum also introduces abundant vacancies and oxygen adsorbed species. Besides, the amorphous nanosheet architecture of the material favours the presence of surface defects and coordinatively unsaturated sites, boosting the exposure of active sites and further improving catalytic activity. Finally, using several pieces of evidence, we revealed the incorporation of molybdenum to enable a LOM, which is in part responsible for the excellent OER performance obtained.

Conflicts of interest

There are no conflicts to declare.

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Article

MOF-Derived Ultrathin Cobalt Molybdenum Phosphide Nanosheets for Efficient Electrochemical Overall Water Splitting

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Abstract: The development of high-performance and cost-effective earth-abundant transition metal-based electrocatalysts is of major interest for several key energy technologies, including water splitting. Herein, we report the synthesis of ultrathin CoMoP nanosheets through a simple ion etching and phosphorization method. The obtained catalyst exhibits outstanding electrocatalytic activity and stability towards oxygen and hydrogen evolution reactions (OER and HER), with overpotentials down to 273 and 89 mV at 10 mA cm⁻², respectively. The produced CoMoP nanosheets are also characterized by very small Tafel slopes, 54.9 and 69.7 mV dec⁻¹ for OER and HER, respectively. When used as both cathode and anode electrocatalyst in the overall water splitting reaction, CoMoP-based cells require just 1.56 V to reach 10 mA cm⁻² in alkaline media. This outstanding performance is attributed to the proper composition, weak crystallinity and two-dimensional nanosheet structure of the electrocatalyst.

Keywords: MOF; phosphide; nanosheet; water splitting



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1. Introduction

Hydrogen, with a high gravimetric energy density (142 MJ kg⁻¹) and zero-carbon emissions, is both a key component in the chemical industry and a very appealing energy carrier for clean and sustainable energy storage and supply [1,2]. Since molecular hydrogen is not freely available in nature, it needs to be extracted from hydrogen-containing compounds. Currently, fossil fuels are the main source of H₂, which involves the release of large amounts of carbon. The electrochemical water splitting is the main green alternative to produce H₂, but it is seriously hampered by the high cost and insufficient durability of current electrocatalysts, based on scarce novel metals such as Pt, Ir and Ru [3–6], and the slow kinetics of the hydrogen and oxygen evolution reactions (HER, OER), which makes water electrolysis not competitive with steam reforming of natural gas or coal gasification processes [7–9].

In order to overcome the current challenges and enable the massive production of H₂ by water splitting, substantial efforts were devoted to the development of high activity, stable and cost-effective electrocatalysts for overall water splitting (OWS). Among the wide range of materials proposed for alkaline water electrolysis, including metal oxides/hydroxides [10–12], chalcogenides [13–16], nitrides [17,18] and carbides [19,20], metal phosphides demonstrated particularly attractive catalytic performances [21,22].

The outstanding performance of phosphides was related to their high electrical conductivity, favorable electronic structure and high stability against corrosion [23,24]. Amongst phosphides, cobalt phosphide (CoP) exhibits an exceptional HER activity associated with a proper electronic structure and specifically to the effective capture of protons by the negatively charged phosphorous atoms [25,26]. Besides, CoP is also characterized by a very high OER activity associated with the high ability of the positively charged cobalt cations to adsorb oxygen intermediates while the negatively-charged P facilitates the desorption of O₂ molecules [27,28]. However, the OWS in CoP still requires too large overpotentials for practical applications, mainly ascribed to the high dissociation energy of water and the sluggish OER kinetics involving a multi-electron transfer process [29,30].

An effective strategy to optimize a material's performance is the introduction of an additional element that provides additional degrees of freedom to modulate its electronic structure and surface properties. Within transition metal phosphide electrocatalysts, additional metals enable a fine-tuning of the d-band position, optimizing the adsorption free energy of the reactants/intermediates/products and thus improving the catalytic activity and even stability. In this direction, Xiao et al. reported the HER catalytic activity of CoP to be boosted by vanadium doping [31]. The introduced V strongly interacts with the hosted Co atoms, enhancing the VCoP electron density and thus accelerating the HER. Other elements, such as Zn [32], Mn [33], Ni [34], Ce [35], Cr [36] and W [21], were also demonstrated to promote either the HER or OER through enhancing electron interactions [28].

Beyond composition, the structure, morphology and organization of the catalyst particles are key parameters defining the density, accessibility and activity of the catalytic sites, which ultimately determine the catalytic activity. In this regard, metal–organic frameworks (MOFs), with a crystalline and porous structure formed by metal ion/cluster bridged by organic ligands, were demonstrated to be excellent sacrificial templates to produce porous carbon-based nanomaterials with tuned composition and morphology [37–40].

Inspired by the above considerations, we rationally designed a novel and highly effective bifunctional electrocatalyst for OWS. This new catalyst is based on CoP, structured as 2D ultrathin nanosheets and derived from the ZIF-67 MOF. It includes Mo⁶⁺ as a high valence 4d transition metal ion, which ionic radius of 0.62 Å matches well with that of Co³⁺ (0.63 Å), thus allowing the substitution of Co³⁺ by Mo⁶⁺ within the CoP lattice [41,42]. We demonstrated here that the proposed porous nanosheet-based structure and the incorporation of Mo within the CoP lattice enable rapid water dissociation and effective and stable HER and OER performances.

2. Materials and Methods

2.1. Chemicals

Ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, 90%), cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, 99.9%), potassium hydroxide (KOH, 85%), iridium(IV) oxide (IrO₂, 99.9% metal basis) and Nafion (5 wt% within a blend of low aliphatic alcohols and water) were obtained from Sigma-Aldrich (St. Louis, MO, USA). 2-Methylimidazole (C₄H₆N₂, 99%) was purchased from Acros Organics (Antwerp, Belgium). Analytical grade methanol, ethanol and isopropanol were obtained from different sources. Milli-Q water was produced using an Elga Purelab flex. All chemicals were used as received.

2.2. Preparation of ZIF-67

ZIF-67 was produced following a previously reported procedure with some modifications [16,43]. Briefly, 0.87 g Co(NO₃)₂·6H₂O was dissolved in 30 mL of methanol to obtain a clear solution. Subsequently, the above solution was poured into 30 mL of methanol containing 1.97 g of 2-methylimidazole under vigorous stirring. After mixing completely, the solution was incubated for 24 h at room temperature. Purple precipitates were collected by centrifugation; they were washed with methanol three times and then dried at 60 °C overnight.

2.3. Preparation of Mo–Co MOFs

One hundred and twenty milligrams of as-prepared ZIF-67 powder was ultrasonically re-dispersed in 20 mL of ethanol. This solution was poured into 100 mL of an aqueous solution containing 50 mg, 100 mg and 200 mg of ammonium molybdate under continuous magnetic stirring. The mixture was then stirred vigorously for 24 h at room temperature. Lavender precipitates were collected by centrifugation, washed with water at least three times and freeze-dried overnight.

2.4. Preparation of CoP and CoMoP

The obtained ZIF-67 and Mo–Co MOFs powders were placed in a porcelain boat within a horizontal tube furnace. In another boat, a 20× mass amount of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ was placed at the upstream side of the tube furnace. The material was then annealed at 350 °C under N_2 flow. After calcination for 2 h, the final black products were denoted as CoP and CoMoP, respectively.

2.5. Structural Characterization

Powder X-ray diffraction (XRD) was performed on a Bruker AXS D8 Advance X-ray diffractometer (Bruker, Billerica, MA, USA) with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Scanning electron microscopy (SEM) analysis was conducted with a Zeiss Auriga microscope (Carl Zeiss, Jena, Germany) equipped with an energy dispersive spectroscopy (EDS) detector operating at 20 kV. Transmission electron microscopy (TEM), High-resolution TEM (HRTEM), Annular dark-field scanning transmission electron microscope (HAADF-STEM) and electron energy loss spectroscopy (EELS) analysis were obtained using a field emission gun FEI Tecnai F20 microscope (FEI, Hillsboro, OR, USA) with a Gatan Quantum filter (Pleasanton, CA, USA) at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a SPECS using an Al anode XR50 source at 150 W and a 150 MCD-9 detector from Phoibos (SPECS, Berlin, Germany).

2.6. Electrochemical Measurements

Electrochemical characterization was performed in a standard three-electrode system using an electrochemical workstation (CHI 760E, CH Instruments, Shanghai, China) in 1 M KOH solution (pH = 14). A graphite rod counter electrode and a Hg/HgO reference electrode were employed. Electrochemical impedance spectroscopy (EIS) was measured within a frequency from 0.01 Hz to 10 kHz at 10 mV amplitude. The initial voltage was fixed at the overpotential required to obtain a current density of 10 mA cm^{-2} . The electrochemically active surface area (ECSAs) was determined using the electrochemical double-layer capacitance (C_{dl}) obtained with cyclic voltammetry data at different scan rates ($v = 20\text{--}100 \text{ mV}\cdot\text{s}^{-1}$). Stability was determined by CV using 3000 cycles at $100 \text{ mV}\cdot\text{s}^{-1}$ and by chronopotentiometry at $10 \text{ mA}\cdot\text{cm}^{-2}$. Overall water splitting tests were carried out in a two-electrode system with the voltage range of 0–2.0 V at a scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$ in 1.0 M KOH electrolyte.

3. Results and Discussion

3.1. Characterization of Electrocatalysts

CoMoP nanosheets were produced by a three-step process involving the synthesis of a Co–MOF, its etching and partial cation exchange and a final phosphorization step, as schematically illustrated in Figure 1a. First, a cobalt-based zeolitic imidazolate framework (ZIF-67), consisting of polyhedral-shaped micrometer-size particles, was produced as a self-sacrificial template (Figure 1b). The ZIF-67 was reacted with ammonium molybdate with the double role of etching the structure and partially replacing Co^{3+} cations by Mo^{6+} , yielding a porous wrinkled nanosheet-based material that we refer to as Co–Mo MOF (Figure 1c). Finally, the Co–Mo MOF was annealed within a tube furnace containing NaH_2PO_2 at 350 °C for 2 h to produce a porous phosphide with a similar wrinkled nanosheet-based morphology that we denoted as CoMoP (Figures 1d and S1). EDS analysis

of CoMoP showed a Co–Mo atomic ratio of $\text{Co}/\text{Mo} = 4$, and a phosphorus–metal atomic ratio of $\text{P}/\text{M} = 2.6$ ($\text{M} = \text{Co} + \text{Mo}$) (Figure S2).

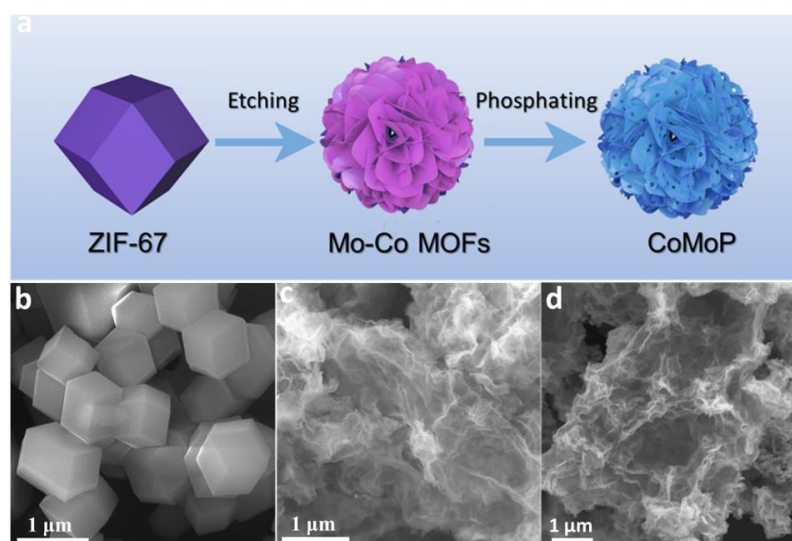


Figure 1. (a) Schematic illustration of the CoMoP synthesis process. (b–d) SEM image of (b) ZIF-67 (c) Mo–Co MOFs and (d) CoMoP.

In order to study the effect of ammonium molybdate, we replaced this chemical with an alternative Mo precursor. Using sodium molybdate as Mo source, the morphology of the final product was much more compact, consisting of partially porous cubes (Figure S3). Besides, EDS analysis revealed the molybdenum content of this material to be much lower ($\text{Co}/\text{Mo} = 18.8$) than that of CoMoP. We will refer to this material as Mo–CoP. As a reference, a Mo-free CoP was obtained by directly annealing the ZIF-67 in the presence of the phosphorous source, with no etching step (Figure S4). The obtained material also displayed a more compact geometry than that of the CoMoP nanosheets.

Figures 2a,b and S5 displays TEM images of CoMoP, further revealing their ultra-thin nanosheet structure. HAADF-STEM analysis and EELS chemical composition maps (Figures 2e, S6 and S7) displayed a homogenous distribution of C, Co, Mo and P within each CoMoP nanosheet. HRTEM images (Figure 2c) and SAED patterns (Figure 2d) showed CoMoP to present a weak crystallinity, with strong middle/long-range disordered [44–46]. In this regard, while the XRD patterns of ZIF-67 and Na_2MoO_4 -ZIF-67 displayed a good crystallinity (Figure 3a), the Co–Mo MOF already presented a mostly amorphous structure. After phosphorization, CoP maintained a relatively well-organized lattice, and CoMoP displayed a weak crystallographic order, consistently with HRTEM results (Figure 3b).

As expected, the XPS survey spectrum displayed the presence of C, N, O, P, Co and Mo elements on the surface of CoMoP (Figure 3c). The high-resolution P 2p XPS spectrum displayed two doublets, which we associated with P within the metal phosphide lattice ($\text{P } 2p_{3/2} = 129.7 \text{ eV}$), and a phosphate chemical environment ($\text{P } 2p_{3/2} = 133.8 \text{ eV}$) (Figure 3d) [41,47]. The Co 2p XPS spectrum displayed six peaks (Figure 3e). The main Co 2p contribution was assigned to Co within the phosphide lattice ($\text{Co } 2p_{3/2} = 779.3 \text{ eV}$). A second doublet was associated with Co within an oxide, hydroxide or phosphate chemical environment ($\text{Co } 2p_{3/2} = 781.5 \text{ eV}$). The last two bands were assigned to satellite peaks [28–30,48,49]. Finally, the Mo 3d XPS spectrum displayed two doublets assigned to Mo within the metal phosphide lattice ($\text{Mo } 3d_{5/2} = 228.2 \text{ eV}$) and an oxidized chemical environment ($\text{Mo } 3d_{5/2} = 233.0 \text{ eV}$) (Figure 3f) [50–52].

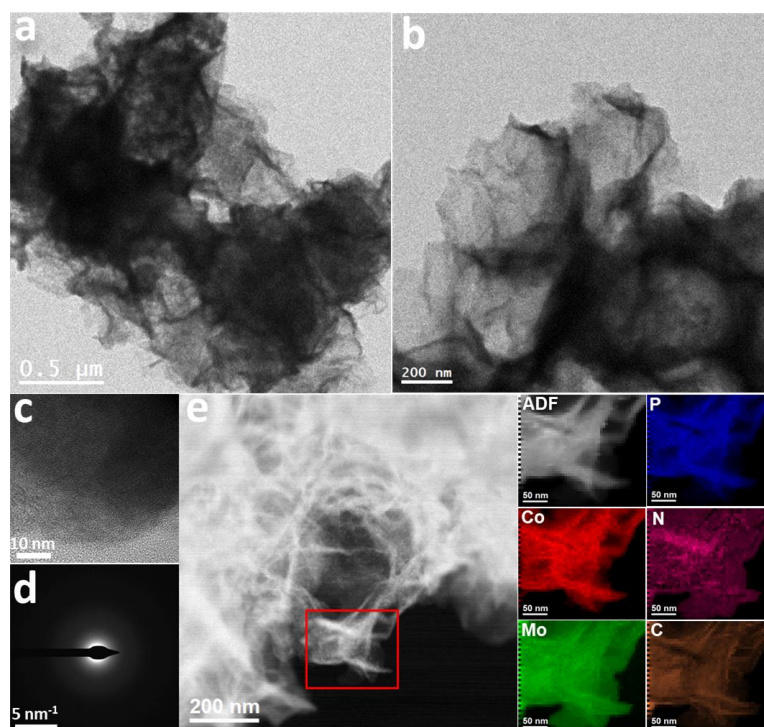


Figure 2. (a,b) TEM images, (c) HRTEM image, (d) SAED pattern and (e) HAADF STEM image and EELS chemical composition maps obtained from the red squared area of the STEM micrograph. Individual Co $L_{2,3}$ edges at 779 eV (red), Mo $M_{4,5}$ edges at 230 eV (green), P $L_{2,3}$ edges at 132 eV (blue), N K edge at 401 eV (pink) and C K edge at 284 eV (orange).

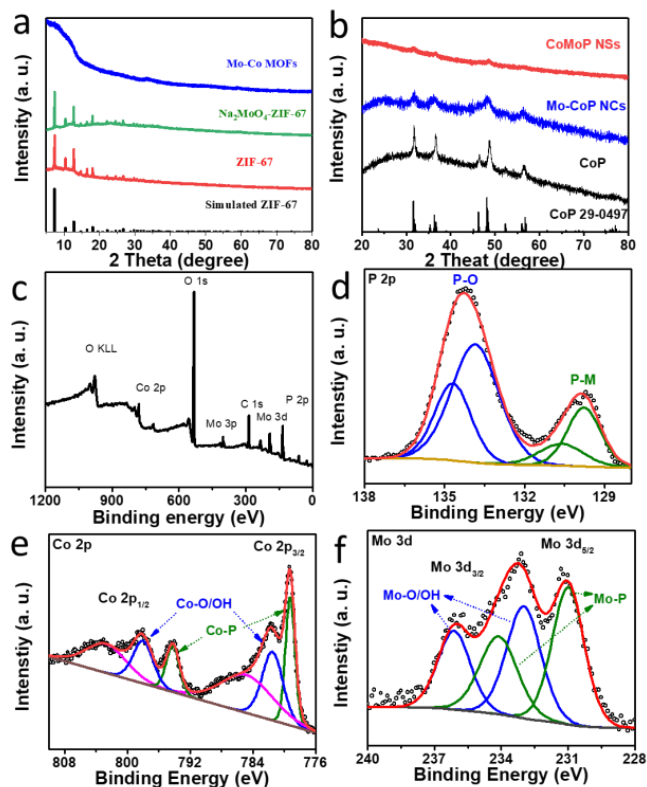


Figure 3. (a,b) XRD pattern of the MOFs (a) and the phosphorized materials, CoMoP, Mo-CoP and CoP. (c–f) XPS survey and high-resolution P 2p (d), Co 2p (e) and Mo 3d (f) XPS spectra of CoMoP.

3.2. Oxygen Evolution Reaction

The OER activity of CoMoP was evaluated at room temperature using a three-electrode system in a 1.0 M KOH alkaline solution. As a reference, Mo–CoP, CoP and a commercial RuO₂ catalyst were also evaluated in the same cell and reaction conditions. The LSV polarization curves displayed the CoMoP to be characterized by an outstanding OER activity, with an overpotential of only 273 mV at a current density of 10 mA cm^{−2} (Figures 4a and S8). This overpotential is well below that of Mo–CoP, CoP and the RuO₂ electrocatalyst tested here and outperforms that of previously reported CoP-based OER catalysts, as shown in Table S1. As displayed in Figure 4b, CoMoP was not only characterized by the lowest overpotential at 10 mA cm^{−2} but also provided the lowest Tafel slope, 54.9 mV dec^{−1}. This value was significantly below that of Mo–CoP (60.4 mV dec^{−1}), CoP (71.5 mV dec^{−1}) and RuO₂ (86.4 mV dec^{−1}), which indicates CoMoP to have associated a faster OER reaction kinetics [53,54].

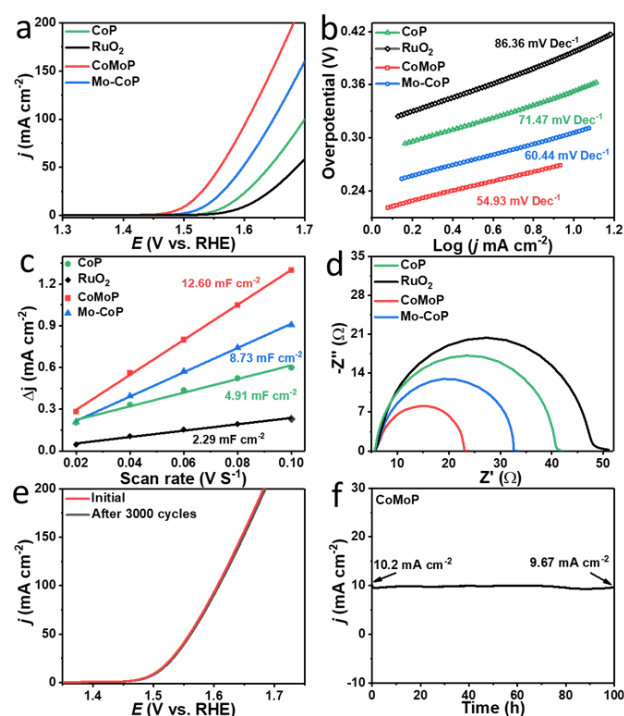


Figure 4. (a) OER polarization curves in 1.0 M KOH. (b) Corresponding Tafel plots. (c) Double-layer capacitances (C_{dl}). (d) Nyquist plots of the EIS data. (e) OER polarization curves before and after 3000 cycles. (f) OER chronoamperometric data for CoMoP at an overpotential of 273 mV.

The electrochemical active areas (ECSA) of CoMoP, Mo–CoP NCs, CoP and RuO₂ were estimated according to the double-layer capacitance (C_{dl}) determined via CV in the non-faradaic region at different scan rates, 20, 40, 60, 80 and 100 mV · s^{−1} (Figures S9 and 4c). CoMoP displayed larger C_{dl} (12.6 mF cm^{−2}) than Mo–CoP (8.7 mF cm^{−2}), CoP (4.9 mF cm^{−2}) and RuO₂ (2.3 mF cm^{−2}). This result indicates that CoMoP offers a higher density of accessible electrochemical active sites, which we relate to the proper composition and nanosheet structure of CoMoP.

The charge transport/transfer ability of the electrocatalysts was evaluated by electrochemical impedance spectroscopy (EIS). An equivalent circuit model including a charge transfer resistance (R_{ct}) and a solution resistance (R_s) during the OER process was used to fit the Nyquist plots displayed in Figure 4d [55,56]. CoMoP exhibited the smallest R_{ct} (17.99 Ω), well below that of Mo–CoP (R_{ct} = 27.90 Ω), CoP (R_{ct} = 36.70 Ω) and RuO₂ (45.47). These results reveal the CoMoP nanosheets to enable a faster charge transfer at the electrode/electrolyte interfaces, thus accelerating the OER electrocatalytic kinetics.

The long-term stability of CoMoP was further analyzed by CV and chronopotentiometry measurements [57,58]. Figure 4e shows how the LSV curve of CoMoP after 3000 CV

cycles closely resembles that of the first cycle. The chronoamperometry test displayed CoMoP to have an outstanding long-term catalytic activity with just a 3% current density decay after 100 h of operation at 273 mV (Figure 4f). SEM images of the post-catalysts after OER testing at high current showed the ultrathin CoMoP nanosheets to partially sinter into a highly porous structure with thicker walls (Figure S10). At the same time, the EDX result showed that a loss of P occurred during the OER. These results are consistent with the reorganization of the metal phosphide into a metal (oxy)-hydroxide during the OER reaction [59,60].

3.3. Hydrogen Evolution Reaction

The HER performance of CoMoP was evaluated in 1.0 M KOH using a three-electrode system, and it was compared with that of Mo-CoP, CoP and a commercial Pt/C catalyst. As shown in Figures 5a and S8b, the CoMoP electrocatalyst displayed a relatively low HER overpotential of 89 mV at the current density of 10 mA cm^{-2} , slightly above that of Pt/C (42 mV) and well below that of Mo-CoP (154 mV), CoP (165 mV) and most previously reported phosphide-based HER electrocatalysts (Table S2). The Tafel slope of CoMoP (69.7 mV dec^{-1}) was also much lower than those of Mo-CoP (83.7 mV dec^{-1}), CoP ($113.4 \text{ mV dec}^{-1}$) and close to that of Pt/C (56.1 mV dec^{-1}) (Figure 5b), which indicated rapid HER reaction kinetics following the Volmer–Heyrovsky mechanism [61,62]. CoMoP also displayed the smallest semicircular diameter in the Nyquist plot of the EIS data among the phosphide catalysts tested (Figure 5c), showing the lowest charge transfer resistance during catalytic processes. In terms of stability under HER conditions, Figure 5d displays how CoMoP suffered a minor change in the LSV curves after 3000 cycles. Additionally, the CA measurement showed the current density to decrease just 6% after 100 h of continuous operation under HER conditions at an overpotential 89 mV (Figure 5e). The morphology and composition of the catalyst after long-term HER are displayed in Figure S11. In this case, minor changes in structure and a moderate P loss were observed, which points to notable catalyst stability under HER.

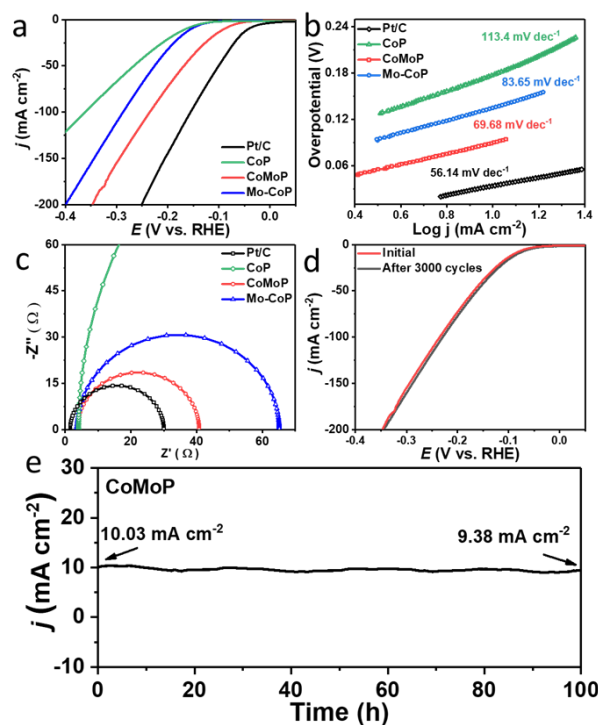


Figure 5. (a) HER polarization curves in 1.0 M KOH. (b) Corresponding Tafel plots. (c) Nyquist plots of the EIS data. (d) HER polarization curves before and after 3000 cycles. (e) Chronoamperometry data for CoMoP at a 89 mV overpotential.

3.4. Overall Water Splitting

Due to the excellent OER and HER performances demonstrated by CoMoP, a two-electrode configuration electrolyzer with CoMoP both as the positive and negative electrodes was constructed and tested for OWS in 1.0 M KOH solution (Figure 6a). As shown from the polarization curves displayed in Figure 6b, the assembled device just required a cell voltage of 1.56 V to reach a current density of 10 mA cm^{-2} , which is significantly below that of a cell containing Pt/C and RuO₂ electrodes (1.61 V). More importantly, after 40 h of continuous operation at 100 mA cm^{-2} , the CoMoP-based cell still maintained an outstanding performance, with just a 14.8% loss at high current density (Figure 6c). Thus, the as-prepared CoMoP can be considered as a highly competitive electrocatalytic catalyst for OWS compared with the previously reported OWS catalysts (Figure 6d, Table S3). Besides, its outstanding stability demonstrates its potential for large-scale hydrogen production from water splitting.

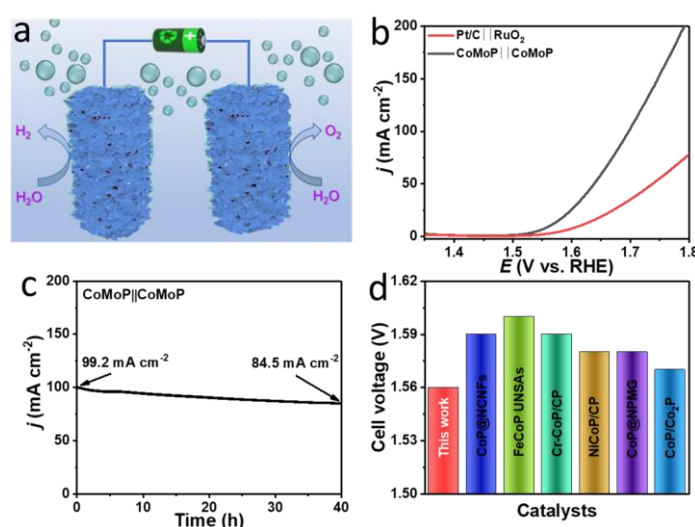


Figure 6. (a) Schematic diagram of the OWS in a two-electrode system. (b) Polarization curves of OWS cells with the electrode pairs: CoMoP | CoMoP and Pt/C | RuO₂ in 1.0 M KOH. (c) Chronoamperometric curve of CoMoP in the two-electrode system at 1.70 V polarization. (d) Comparison of the CoMoP overpotential at 10 mA cm^{-2} with previously reported catalysts in 1.0 M KOH.

4. Conclusions

In conclusion, ultrathin CoMoP nanosheets were engineered using the Co-MOF ZIF-67 as a self-sacrificial template and ammonium molybdate as a shape-defining agent and Mo source. CoMoP nanosheets exhibited outstanding performance towards HER and OER in alkaline media, which we associate with the proper transport properties and electronic energy levels provided by their composition and their porous nanosheet structure. In particular, CoMoP presented low overpotentials of 89 and 273 mV at a current density of 10 mA cm^{-2} for HER and OER, respectively. Furthermore, CoMoP electrocatalysts also showed excellent long-term stabilities in alkaline electrolytes, with a minor current density decrease after 100 h continuous operation. When used for OWS, a cell voltage of only 1.56 V was needed to reach a current density of 10 mA cm^{-2} . This work provides a suitable strategy to synthesize high-performance Co-Mo-P electrocatalysts with abundant exposed active sites and effective avenues for charge and electrolyte transport, and it can be employed to further tune the structure and composition of other 2D nanostructures with optimized performance towards OWS and other electrocatalytic reactions.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/nano12071098/s1>, Figure S1: (a–f) SEM images of CoMoP; Figure S2: (a) SEM images of Co-Mo MOFs. (b,c) SEM images and (d) EDX spectrum of CoMoP. Figure S3: (a) SEM images of Na₂MoO₄-ZIF-67. (b,c) SEM images and (d) EDX spectrum Mo-CoP; Figure S4:

(a) SEM images of ZIF-67. (b,c) SEM images and d) EDX spectrum CoP. Figure S5: (a–d) TEM image of CoMoP. Figure S6: (a–d) HAADF-STEM micrographs of CoMoP. Figure S7: EELS chemical composition maps obtained from the red squared area of the STEM micrograph. Individual Co L_{2,3}-edges at 779 eV (red), Mo M_{4,5}-edges at 230 eV (green), P L_{2,3}-edges at 132 eV (blue), N K-edge at 401 eV (pink) and C K-edge at 284 eV (orange). Figure S8: (a) OER and (b) HER polarization curves of CoMoP with different Mo content in 1.0 M KOH. Figure S9: Cyclic voltammograms for (a) CoMoP; (b) Mo–CoP; (c) CoP and (d) RuO₂ in the non-faradaic region of 1.12–1.22 V vs. RHE at various scan rates. Figure S10: (a–c) SEM image and (d) EDX spectrum of CoMoP after long-term OER stability testing. Figure S11: (a–c) SEM image and (d) EDX spectrum of CoMoP after long-term HER stability testing. Table S1: Comparison of OER performance of CoMoP with some previously reported CoP-based catalysts in 1.0 M KOH solution. Table S2: Comparison of HER performance of CoMoP with some previously reported CoP-based catalysts in 1.0 M KOH solution. Table S3: Comparison of OWS performance of CoMoP with some previously reported CoP-based catalysts in 1.0 M KOH solution. References [63–81] are cited in the supplementary materials.

Author Contributions: The manuscript was prepared through the contribution of all authors. A.C. guided the project and supervised the work. X.W., L.Y., C.X., R.D., R.H. and P.G. conceived and prepared the manuscript. X.W. and L.Y. produced the samples. X.W. and C.X. performed the electrochemical measurements and analyzed the results. X.H., J.A. and P.G. performed TEM, HRTEM and discussed these results. X.W. and R.H. performed XPS measurements and discussed these results. The manuscript was corrected and improved by all authors. All authors have read and agreed to the published version of the manuscript.

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Electrochemical reforming of ethanol with acetate Co-Production on nickel cobalt selenide nanoparticles

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ABSTRACT

The energy efficiency of water electrolysis is limited by the sluggish reaction kinetics of the anodic oxygen evolution reaction (OER). To overcome this limitation, OER can be replaced by a less demanding oxidation reaction, which in the ideal scenario could be even used to generate additional valuable chemicals. Herein, we focus on the electrochemical reforming of ethanol in alkaline media to generate hydrogen at a Pt cathode and acetate as a co-product at a $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$ anode. We first detail the solution synthesis of a series of $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$ electrocatalysts. By adjusting the Ni/Co ratio, the electrocatalytic activity and selectivity for the production of acetate from ethanol are optimized. Best performances are obtained at low substitutions of Ni by Co in the cubic NiSe_2 phase. Density function theory reveals that the Co substitution can effectively enhance the ethanol adsorption and decrease the energy barrier for its first step dehydrogenation during its conversion to acetate. However, we experimentally observe that too large amounts of Co decrease the ethanol-to-acetate Faradaic efficiency from values above 90% to just 50%. At the optimized composition, the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ electrode delivers a stable chronoamperometry current density of up to 45 mA cm^{-2} , corresponding to 1.2 A g^{-1} , in a $1 \text{ M KOH} + 1 \text{ M ethanol}$ solution, with a high ethanol-to-acetate Faradaic efficiency of 82.2% at a relatively low potential, 1.50 V vs. RHE , and with an acetate production rate of $0.34 \text{ mmol cm}^{-2} \text{ h}^{-1}$.

1. Introduction

Molecular hydrogen is a convenient carbon-free energy carrier and a key component in the chemical industry. While molecular hydrogen does not exist in nature, it can be produced by water electrolysis using renewable energy sources such as wind, hydropower, and solar.[1] However, while water electrolysis systems have been commercialized for several years, their high cost has prevented extensive deployment, and most molecular hydrogen is still being produced by the partial oxidation and steam reforming of natural gas and coal gasification.[2] To turn this trend around, cost-effective strategies for the production of hydrogen from renewable sources need to be developed. In this context, biomass-derived products provide an excellent alternative source of

hydrogen owing to their renewable character and their net-zero CO_2 footprint.[3] Besides, the partial oxidation of an organic molecule offers a less energy demanding anodic oxidation reaction, which can contribute to overcoming the energy efficiency limitation of water electrolysis associated with the sluggish reaction kinetics of the oxygen evolution reaction (OER).[4–6] An additional advantage of the production of hydrogen from the reforming of waste or biomass-derived organics is the potential co-generation of valuable organic chemicals, which can both improve process economics and further diminish the dependence on fossil resources that are currently used to produce them.[7–9] On top of these advantages, the replacement of OER by an organic oxidation reaction enables the implementation of coupled cost-effective waste abatement processes. Thus, overall, the clean electrochemical

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conversion of organic waste and biomass-derived products into value-added chemicals driven by renewable energy has both high fundamental interest and enormous potential for socio-economic and environmental impact. [10–13].

In this scenario, (bio)ethanol is a paradigmatic and particularly interesting hydrogen source. Ethanol is a key commodity in the chemical industry, used as a precursor or building block for the synthesis of a plethora of chemicals, including formaldehyde, acetic acid, and plastics. [14,15] Ethanol can be renewably generated from the reduction of CO₂ and several biomass-derived feedstocks and organic residues such as sewage sludge. [12–14] As a liquid, ethanol can be easily stored and transported. Besides, bioethanol aqueous solutions can be directly used in electrocatalytic processes, without the need for purification. Compared with water splitting, the production of hydrogen from ethanol is thermodynamically advantageous ($\Delta G^0 = +237 \text{ kJ}\cdot\text{mol}^{-1}$ for water oxidation vs. $\Delta G^0 = +9.6 \text{ kJ}\cdot\text{mol}^{-1}$ for ethanol oxidation to acetate), which decreases the energy input required. [16] The reforming of ethanol also prevents the H₂ and O₂ back reaction. Besides, compared with the complete ethanol reforming down to CO₂, the production of H₂ and acetate could have higher economical profitability associated with the high economic value of acetate as a side product. [17].

In terms of catalysts, while OER generally requires high-cost noble metal electrocatalysts, the electrooxidation of organic molecules, such as methanol or ethanol, in alkaline media can be activated at a lower cost using abundant 3d transition metal-based electrocatalysts, e.g. nickel, iron and cobalt. [17–19] To improve the electrocatalytic performance, multimetallic transition metal-based nanoparticles have been also developed and studied. Among them, nickel–cobalt compounds have demonstrated particularly high activity towards OER, [20–22] and excellent performance for the conversion of methanol to formate, [23–26]. Thus, we hypothesize nickel–cobalt selenides to be excellent electrocatalysts for the ethanol oxidation catalysts, but this reaction and its mechanism is yet to be studied on these materials.

Herein, we detail the preparation of bimetallic Ni-Co selenides nanoparticles (NPs) over a full range of compositions using a solution-based strategy. This set of materials is tested for the partial electro-oxidation of ethanol in an alkaline electrolyte. Finally, the material is optimized to minimize the overpotential and maximize the activity and Faradaic efficiency for ethanol to acetate conversion.

2. Experimental section

2.1. Chemicals

All chemicals, including cobalt(II) acetylacetonate (Co(acac)₂, 97%, Sigma Aldrich), selenium powder (Se, 200 mesh, 99.5%, Acros Organics), nickel(II) acetylacetonate (Ni(acac)₂, 96%), oleylamine (OAm, C₁₈H₃₇N, 80–90%, Acros Organics), potassium hydroxide (KOH, 85%, Sigma Aldrich), potassium carbonate (K₂CO₃, 99.5%, Sigma Aldrich), potassium bicarbonate (KHCO₃, 99.7%, Sigma Aldrich), 1,2-ethanedithiol (EDT, HSCH₂CH₂SH, 98%, Sigma Aldrich), oleic acid (OAc, C₁₈H₃₄O₂, 99%, Sigma Aldrich), carbon black (CB, Vulcan XC72, Sigma Aldrich), and Nafion (10 wt%, perfluorinated ion-exchange resin, dispersion in water, Sigma Aldrich), were used as received, without further treatment. Analytical grade chloroform and ethanol for the washing process were obtained from various sources. MilliQ water (18.2 MΩ·cm) was used for electrolyte and ink preparation, and ion chromatography (IC) measurements. An argon-filled glove box was used to handle sensitive chemicals and for ink preparation.

2.2. Solution-based synthesis of Ni_{1-x}Co_xSe₂ NPs

Bimetallic selenide NPs were produced from a two-step process involving the preparation of a reactive ink and its decomposition. First, the precursor ink was prepared inside an argon-filled glove box by dissolving (1-x) mM of Ni(acac)₂, x mM of Co(acac)₂, and 8 mM of Se

powder inside a vial with 30 mL of OAm and 3 mL of EDT under vigorous stirring for 1 h at 50 °C. The introduction of EDT was required to dissolve the Se powder. The obtained solution was then filtered through a 0.2 μm filter. Then, 36 mL of the prepared precursor together with 60 mL of OAm and 30 mL OAc were placed in a 250 mL three-neck flask and vacuumed at 60 °C for 30 min followed by heating to 220 °C under Ar at a rate of 5 °C/min. After reacting for 20 min, the solution was rapidly cooled down to room temperature in a water bath. Next, the crude solution was mixed with 60 mL of chloroform and then centrifuged at 8000 rpm for 5 min. The washing process was repeated by dispersion in chloroform/ethanol and centrifugation several times. Finally, the obtained product was stored in chloroform and stored in the glovebox.

2.3. Material characterization

Laboratory X-ray diffraction (XRD) was performed on a Bruker AXS D8 Advance (Cu K radiation: $\lambda = 1.5106 \text{ \AA}$) to study the crystal structure. Scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) measurements were conducted on a Gemini 300 field emission scanning electron microscope (Zeiss, Germany) equipped with an AZtecOne UltimMax40 energy spectrometer. High-resolution transition electron microscopy (HRTEM) and scanning TEM (STEM) investigation were performed on a field emission gun FEI Tecnai F20 microscope. High angle annular dark-field (HAADF) STEM was combined with electron energy loss spectroscopy (EELS) in the Tecnai microscope using a Gatan Quantum filter. The materials' pore size distribution and specific surface area were analyzed by means of N₂ adsorption on a ASAP 2460 Micromeritics system. Specific surface areas were determined by means of the Brunauer – Emmett – Teller (BET) approach, considering equally spaced points in the P/P₀ range. The pore size distribution was calculated from the isotherms desorption branches using the Barrett – Joyner – Halenda (BJH) model. X-ray photoelectron spectroscopy (XPS) analyses were conducted on a Specs system.

2.4. Electrochemical characterization

Electrochemical tests were carried out on a Bio-logic SP-200 potentiostat using a conventional three-electrode system including a Pt wire as the counter electrode, a Hg/HgO reference electrode, and the Ni_{1-x}Co_xSe₂ NPs supported on CB on top of a 5 mm diameter glassy carbon (GC) as working electrode (WE). To prepare the WE, a catalytic ink was prepared by dispersing 3 mg of dried NPs and 6 mg of CB in a vial containing 1.8 mL of MilliQ water/ethanol (v/v = 1:1) and 100 μL of a 10 wt% Nafion solution, followed by half-an-hour of vigorous sonication. Afterwards, 5 μL of this ink were drop-casted on a carefully polished GC electrode and dried naturally in air. Before the measurement, the alkaline electrolyte was bubbled with high-purity N₂ gas for half an hour. Cyclic voltammetry (CV) and chronoamperometry (CA) were applied to study the electrocatalytic performance. To analyze the product of the oxidation reaction at the anode and calculate the ethanol-to-acetate faradaic efficiency, 0.5 mL of the solution was collected, diluted 20-fold with MilliQ water, and then analyzed by IC. A freshly prepared 4.5 mM KCO₃ and 0.8 mM KHCO₃ solution was used as leachate solution for the measurement. The amount of product was quantified with a standard curve obtained from known acetate concentrations. At the cathode, the generated hydrogen was determined by gas chromatography (GC, 8890, Agilent Technologies) connected to the electrocatalytic cell. Before measurement, a stable flow rate of 20 cm³ min⁻¹ Ar (99.999%) was bubbled for 30 mins at the Pt wire in an H-type two-compartment cell, which is separated by a Nafion-115 proton membrane. The GC product analysis was conducted every 12 mins. The produced gas was identified and quantified by a calibration curve using known concentrations of standard H₂ gas. All obtained potentials (vs. Hg/HgO) were converted to the reversible hydrogen electrode (RHE) reference according to the Nernst equation: $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059x \text{ pH} + E_{\text{Hg/HgO}}^0$, where $E_{\text{Hg/HgO}}$ is the measured potential, $E_{\text{Hg/HgO}}^0$ is the

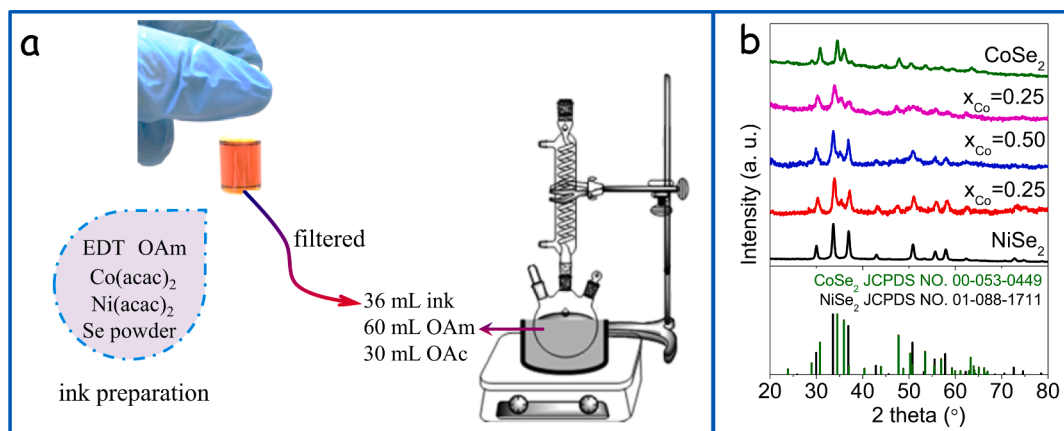


Fig. 1. (a) Schematic drawing of the solution-based process used to produce Ni_{1-x}Co_xSe₂ NPs. (b) XRD pattern of the as-synthesized product.

reference potential of 0.098 V, and pH is 13.6 as it corresponds to the 1.0 M KOH solution. All current densities were referred to the geometrical area of the GC electrode, i.e. 0.196 cm².

2.5. Computational method

The Vienna ab initio package (VASP) was used to perform all the density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the PBE formulation. [27–29] The projected augmented wave (PAW) potential was used to describe the ionic cores and valence electrons were taken into account using a plane wave basis set with a kinetic energy cutoff of 400 eV. [30,31] Partial occupancies of the Kohn – Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than 10⁻⁵ eV. A geometry optimization was considered convergent when the force change was smaller than 0.02 eV/Å. Grimme's DFT-D3 methodology was used to describe the dispersion interactions. [32].

Using a 7 × 11 × 9 Monkhorst-Pack k-point grid for Brillouin zone sampling, the equilibrium lattice constants of the monoclinic NiOOH unit cell were optimized to be a = 5.168 Å, b = 2.847 Å, c = 4.516 Å, at

α = 90°, β = 107.1°, γ = 90°. They were used to construct a NiOOH(001) surface model (model 1) with p(2 × 3) periodicity in the x and y directions and 1 stoichiometric layer in the z direction separated by a vacuum layer in the depth of 15 Å to separate the surface slab from its periodic duplicates. In another model (model 2), three Co atoms were doped into model 1 by replacing three Ni atoms. One O atom was removed from both models to create an oxygen vacancy. During structural optimizations, the gamma point in the Brillouin zone was used for k-point sampling, and all atoms were allowed to relax.

The free energy of a gas phase molecule or an adsorbate on the surface was calculated by the equation G = E + ZPE – TS, where E is the total energy, ZPE is the zero-point energy, T is the temperature in kelvin (298.15 K), and S is the entropy.

3. Results and discussion

3.1. Characterization of catalysts

Ni_{1-x}Co_xSe₂ NPs were produced through a two-step process involving the preparation of a reactive ink from the dissolution of Se and the proper amount of Ni and Co precursors in EDT and OAm and its posterior

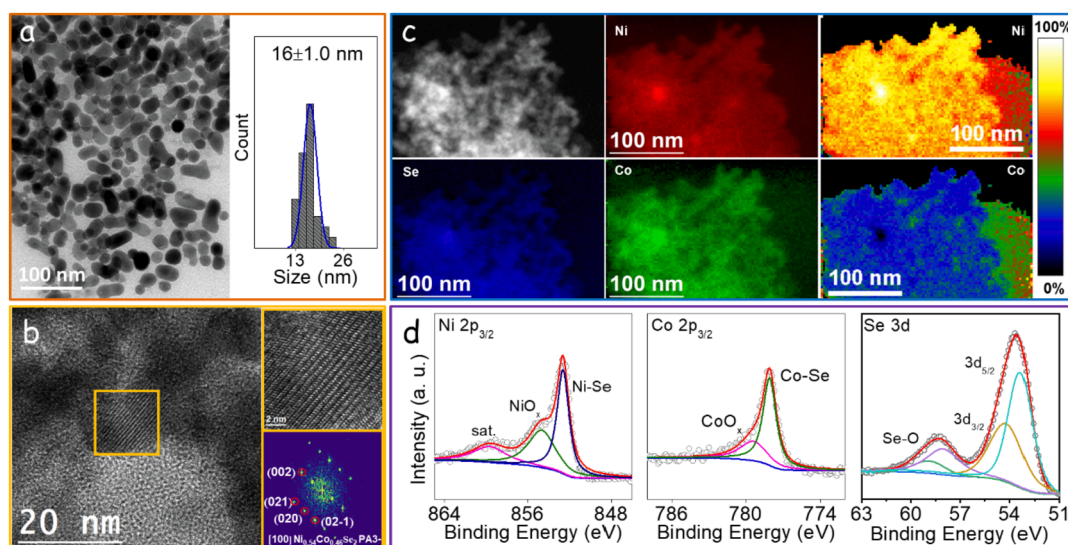


Fig. 2. TEM and XPS characterization of Ni_{0.75}Co_{0.25}Se₂ NPs. (a) TEM image and size distribution histogram. (b) HRTEM micrograph and indexed power spectra. (c) HAADF STEM image and EELS-STEM compositional maps obtained from HAADF STEM shown region. Individual Ni L2,3-edges at 855 eV (red), Co L2,3-edges at 779 eV (red), and Se M1-edges at 231 eV (blue) composition maps. Colour gradient maps display the relative compositions of Ni and Co. The colour scale is the same for both panels (Ni and Co). (d) Ni 2p_{3/2}, Co 2p_{3/2}, and Se 3d high resolution XPS spectra. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

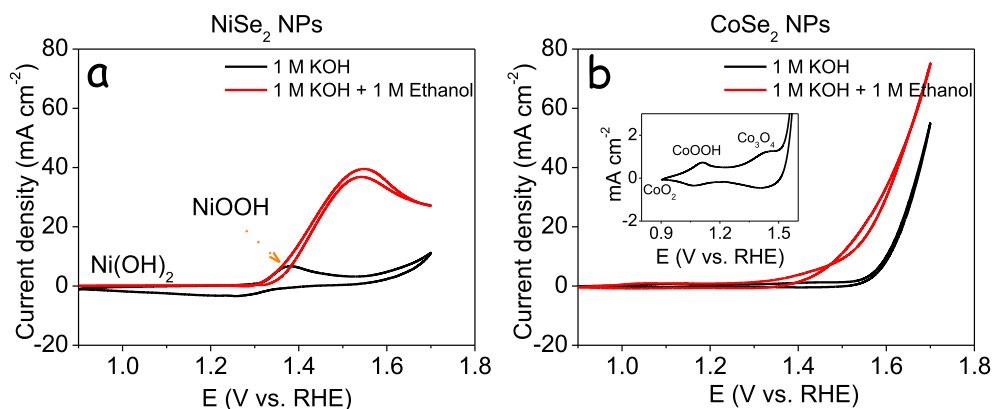


Fig. 3. CV curves of (a) NiSe₂ NP-based electrodes, and (b) CoSe₂ NP-based electrodes within an electrolyte containing a 1 M KOH (black curve) and a 1 M KOH + 1 M ethanol (red curve). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

reaction (see the experimental section for details and Fig. 1a). Fig. 1b displays the XRD patterns of the obtained Ni_{1-x}Co_xSe₂, with $0 \leq x \leq 1$. For $x = 0$ and $x = 1$, the crystal structures of NiSe₂ and CoSe₂ could be properly indexed with the cubic pa-3 (JCPDS No. 01 088 1771) and the

orthorhombic pnnm (JCPDS No. 00 053 0449) phases, respectively. With increasing amounts of Co within the NiSe₂ structure, a continuous transition from the cubic NiSe₂ phase to the orthorhombic CoSe₂ structure was observed. Within the experimental error, SEM-EDS

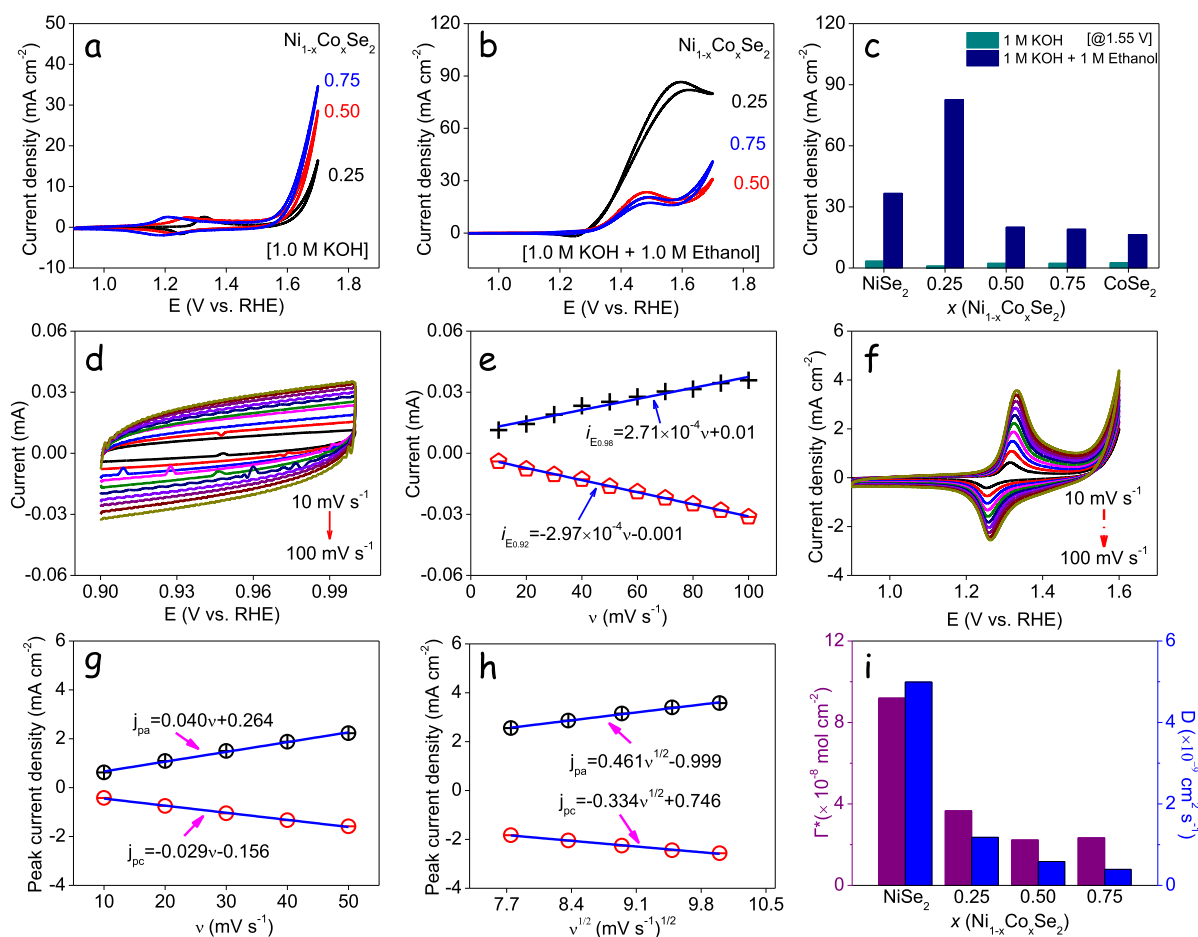


Fig. 4. (a) CV curves for the Ni_{1-x}Co_xSe₂ ($x = 0.25; 0.50; 0.75$) electrodes in 1 M KOH electrolyte in the potential range from 0.9 V to 1.7 V with a scan rate of 50 mV s⁻¹. (b) CV curves in 1 M KOH + 1 M ethanol electrolyte. (c) Current densities in 1 M KOH (green) and 1 M KOH + 1 M ethanol electrolyte (blue) at 1.55 V vs. RHE. (d) CV curves of Ni_{1-x}Co_xSe₂ ($x = 0.25$) based electrode in 1.0 M KOH in the non-Faradaic potential range (0.9–1.0 V) with a scan rate of 10–100 mV s⁻¹. (e) Linear fit of the forward current at 0.98 V and backward current at 0.92 V as a function of scan rate, from 10 to 100 mV s⁻¹. (f) CV curves of a Ni_{1-x}Co_xSe₂ ($x = 0.25$) electrode in the potential range from 1.0 V to 1.60 V with a variable scan rate, from 10 to 100 mV s⁻¹. (g) Linear fit of the peak current and scan rate from 10 to 50 mV s⁻¹. (h) Linear fit of the peak current and square root of scan rate 60 to 100 mV s⁻¹. (i) Comparison of the surface coverage of redox species (Γ^*) and diffusion coefficient (D) for the Ni-containing Ni_{1-x}Co_xSe₂ NPs based electrode in 1 M KOH solution. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

analyses showed the composition of the obtained materials to be consistent with the nominal Ni/Co ratios (Fig. S1). Thus, in the following, we refer to the different samples using the nominal values.

Fig. 2a displays a representative TEM micrograph of the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ sample. It consists of NPs having an average diameter of around 16 nm. When varying the Co composition over the entire Ni/Co range, the NPs size remained unchanged (Fig. S2). HRTEM micrographs show the NPs to be highly crystalline (Fig. 2b). The lattice parameter of the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ NPs is $a = b = c = 5.840 \text{ \AA}$, which is in between that of the NiSe_2 cubic phase ($a = b = c = 5.973 \text{ \AA}$) and the CoSe_2 cubic phase ($a = b = c = 5.681 \text{ \AA}$), in good agreement with a lattice containing a mixture of both cations $\text{Ni}_x\text{Co}_{1-x}\text{Se}_2$. According to Vegard's law, and considering a linear approximation, the amount of Co present in the structure is estimated at $x = 0.46$ for the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ sample. The composition deviation obtained from Vegard's law can be attributed to the different bonding forces of Ni and Co with selenium within the selenide.[33] As can be seen in the EELS compositional maps (Fig. 2c), the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ NPs display a homogeneous distribution of the three elements, with an average ratio $\text{Ni/Co} = 7/3$, consistent with the nominal composition and EDS data. The adsorption – desorption isotherms obtained from the as-prepared NiSe_2 and $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ NPs are displayed in Fig. S3. BET specific surface areas of 6.2 and $6.9 \text{ m}^2 \text{ g}^{-1}$ were calculated for NiSe_2 and $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ NPs, respectively. Besides, the average pore diameter obtained by the BJH model was 45.4 and 51.3 Å for NiSe_2 and $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ NPs, respectively (Fig. S3bd).

XPS analysis was used to characterize the surface composition and element oxidation state (Fig. 2d and Fig. S4). Fig. 2d displays the high resolution Ni 2p_{3/2}, Co 2p_{3/2}, and Se 3d XPS spectra of $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ NPs. Each of the three elements presents two chemical states that we associate with a metal selenide and a metal oxide environment, in good agreement with previous publications including an XPS characterization of nickel- and cobalt- selenides.[34,35] Specifically, aside from a satellite peak at 859.8 eV, the Ni 2p_{3/2} region shows the presence of two chemical states that we associate with Ni ions within Ni-Se (852.6 eV) and within Ni-O (854.7 eV) chemical environments.[36] The Co 2p_{3/2} region also shows two chemical environments associated with Co-Se (778.0 eV) and Co-O (779.4 eV).[37] Finally, the Se 3d XPS spectrum shows a component at 53.4 eV associated with a metal selenide environment and a component at 58.4 eV associated with a selenium oxide environment.[38] The surface oxide component was attributed to the partial oxidation of the NPs surface during XPS sample preparation and transportation.[39].

3.2. Electrocatalytic performance

Working electrodes were prepared by coating a glassy carbon with a catalyst ink prepared by mixing dried NPs and CB in an ethanol/water solution containing Nafion. The electrochemical performance was explored in a conventional three-electrode electrochemical cell using a Pt wire as the counter electrode and a Hg/HgO reference electrode (see the experimental section for details).

First, NiSe_2 - and CoSe_2 -based electrodes were tested in the potential window 0.9–1.7 V vs. RHE with a scan rate of 50 mV s^{-1} in 1 M KOH electrolyte solution. In a basic solution, a hydroxide is formed on the surface of Ni oxides and Ni chalcogenides.[40] As shown in Fig. 3a, during the forward scan, the first current density peak measured from NiSe_2 -based electrodes (black curve) was attributed to the oxidation of surface Ni(OH)_2 to NiOOH at around 1.392 V vs. RHE. At higher applied potential, above ca. 1.65 V vs RHE, a rise in the current density was associated with the OER. During the reverse scan, NiSe_2 -based electrodes displayed a NiOOH to Ni(OH)_2 reduction peak at around 1.380 V vs. RHE.

For the CoSe_2 -based electrode in 1 M KOH solution (black curve in Fig. 3b), two small current density peaks in the forward scan were observed. In an alkaline medium, the surface of Co-based chalcogenides is generally oxidized.[24,41,42] During the forward scan, the surface

cobalt oxide is further oxidized probably to CoOOH at 1.11 V vs. RHE. At ca. 1.439 V vs RHE, CoOOH is even further oxidized, possibly to CoO_2 . These phases are reduced during the reverse scan. At ca. 1.60 V vs. RHE, the OER is activated on the CoSe_2 -based electrode, showing a significantly higher OER activity than the NiSe_2 -based electrode. Upon adding 1 M ethanol to the electrolyte solution, a sharp rise in the current density (red curves in Fig. 3) and corresponding to the ethanol oxidation reaction (EOR) was measured at ca. 1.35 V for both NiSe_2 - and CoSe_2 -based electrodes. Above the OER onset potential, both reactions, OER and EOR, compete with each other [43–45].

Fig. 4 displays the results from the electrochemical characterization of the electrodes based on ternary chalcogenides, $\text{Ni}_{1-x}\text{Co}_x\text{Se}_2$. In a 1 M KOH solution, we observed the OER activity to increase with the amount of Co. Specifically, as shown in Fig. 4a, the potential required to generate 10 mA cm^{-2} decreased from 1.698 V for NiSe_2 , to 1.672 V for $x = 0.25$, 1.638 V for $x = 0.50$, and 1.620 V for $x = 0.75$. These values were still above that of CoSe_2 electrodes, 1.599 V (Table S1).

When adding 1 M ethanol to the electrolyte, a rapid current density increase at lower potentials was observed. In contrast with the OER, the overpotential for EOR at 10 mA cm^{-2} did not follow a monotonous trend with the Co introduction, but we observed the addition of a small amount of Co to result in the highest improvement of the results obtained for NiSe_2 (Fig. 4b and Table S1). Fig. 4c compares the current density of the different electrodes at a fixed potential, 1.55 V, significantly below the OER onset potential. After subtracting the current density measured in 1 M KOH solution, the net EOR current density increased from 33.3 mA cm^{-2} for NiSe_2 , to 81.6 mA cm^{-2} for $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$, and decreased at higher Co concentrations. Changing the scan rate in the range $10\text{--}100 \text{ mV s}^{-1}$, similar CV curves were obtained for $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ -based electrode in the solution containing 1 M KOH and 1 M ethanol, with a nearly unchanged current density at 1.55 V (Fig. S5). If considering the loading mass of NPs, the highest mass current density at 1.55 V was also obtained for the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ electrode, 2.1 A mg^{-1} , and it was significantly above that of recently reported Ni NPs/C,[46] Co_3O_4 nanosheets,[47] CoNi hydroxide nanosheets,[48] and fluorine-modified FeOOH ,[49] and comparable to that of phosphine doped CoS_2 ,[50] Ni-Fe phosphide and Co_3S_4 nanosheets (Table S2). [26,51].

As shown in Fig. 4d, a double-layer pattern for $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ NPs was obtained in 1 M KOH in the potential window of 0.9 V–1.0 V from 10 mV s^{-1} to 100 mV s^{-1} . The electrochemical double-layer capacitance (C_{dl}) in the non-faradaic region was calculated from the linear fit of the current (i) with the scan rate (ν):

$$i_c = \nu C_{dl}$$

From this capacitance, the electrochemical active area (ECSA) was determined using the following equation:

$$ECSA = C_{dl}/C_s$$

where C_s is 0.04 mF cm^{-2} , according to the values reported for Ni-based electrodes in alkaline solution.[52] By averaging the slope obtained from the forward scan at 0.98 V and backward scan at 0.92 V (Fig. 4e), the calculated ECSA for $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ was $90.1 \text{ cm}^2 \text{ g}^{-1}$, well above the values obtained for NiSe_2 ($75.7 \text{ cm}^2 \text{ g}^{-1}$), $\text{Ni}_{0.50}\text{Co}_{0.50}\text{Se}_2$ ($71.0 \text{ cm}^2 \text{ g}^{-1}$), and $\text{Ni}_{0.25}\text{Co}_{0.75}\text{Se}_2$ ($49.7 \text{ cm}^2 \text{ g}^{-1}$) electrodes (Fig. S6 and Table S1). It should be noted that to determine ECSA, the same value of the specific capacitances was used for all compositions, which is a rough approximation that can account for a part of the ECSA variations observed.[53].

The CV curves of the bimetallic selenides displayed just one peak in the forward scan and one peak in the reverse scan (Fig. S7). The peak current density for the bimetallic selenides was found at lower potentials than for NiSe_2 (1.381 V) and the peak potential decreased with the amount of Co introduced, from 1.371 for NiSe_2 to 1.209 V for $\text{Ni}_{0.25}\text{Co}_{0.75}\text{Se}_2$. On the other hand, the voltage of the peak current density in the backward scan did not change monotonically with the amount of Co

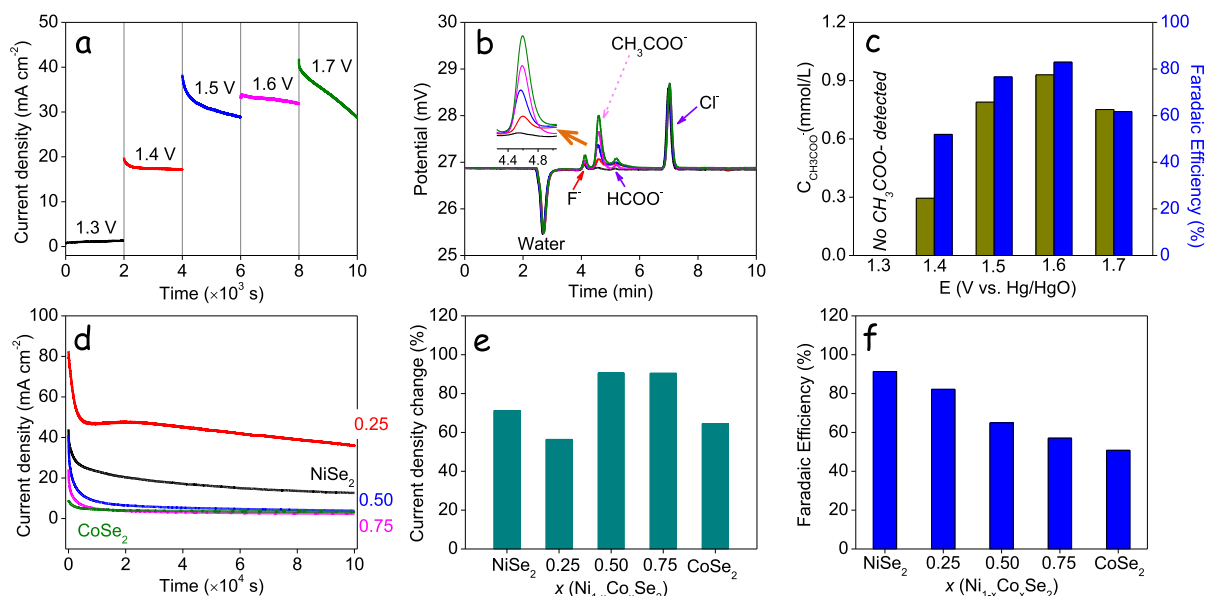


Fig. 5. Electrochemical performance of the bimetallic selenide electrode in 1 M KOH + 1 M ethanol. (a) CA curves of continuous 2,000 s operation for $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ NPs at each potential of 1.3, 1.4, 1.5, 1.6, and 1.7 V. (b) IC profile at the end of each 2,000 s intervals. Inset shows the peaks at 4.6 min obtained at each potential. Black, red, blue, pink, and green curves were recorded at the 2000th, 4000th, 6000th, 8000th, and 10000th s respectively. (c) Calculated acetate concentration and Faradaic efficiency after 2,000 s testing at each potential for $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$. (d) CA curves for the selenide over the entire composition range at 1.50 V for 10,000 s testing. (e, f) Corresponding current density change and faradaic efficiency. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

introduced, but it increased from NiSe_2 (1.219 V) to $\text{Ni}_{0.25}\text{Co}_{0.75}\text{Se}_2$ (1.249 V) and decreased at higher Co concentrations. Associating these peaks to the $\text{Ni}(\text{OH})_2 \leftrightarrow \text{NiOOH}$ redox reaction, we observed the potential difference ΔE_p between the oxidation and reduction peaks decreased from 162 mV for NiSe_2 to 79, 40, and 20 mV with an increasing amount of Co. The smaller potential differences are related to the improved electron transfer kinetics between the electrode surface and the active centres, associated with the modified electronic structure of the bimetallic selenides.[54].

The surface coverage of $\text{Ni}(\text{OH})_2/\text{NiOOH}$ redox species was determined from the dependence of the peak current density on the scan rate. Fig. 4h shows CV profiles from the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ electrode in 1 M KOH solution at 10–100 mV s^{-1} . The redox peak associated with the $\text{Ni}(\text{OH})_2 \leftrightarrow \text{NiOOH}$ redox reaction can be observed in the positive and negative scans. From the linear relationship between the peak current density and the scan rate from 10 to 50 mV s^{-1} , the surface coverage of $\text{Ni}(\text{OH})_2/\text{NiOOH}$ redox species (Γ^*) was determined using the following equation:

$$I_p = \left(\frac{n^2 F^2}{4RT} \right) A \Gamma^* \nu$$

where n is the number of transferred electrons (assumed to be 1 for $\text{Ni}(\text{OH})_2/\text{NiOOH}$), F is the Faraday constant ($96,485 \text{ C mol}^{-1}$), R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the absolute temperature (295 K) and A is the geometric surface area of the GC electrode (0.196 cm^2). Γ^* was calculated considering the average of the fitted slopes for the anodic and cathodic peaks. As expected, the surface coverage of redox species, Γ^* , measured for the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ electrode, $3.7 \times 10^{-8} \text{ mol cm}^{-2}$, was well below that of NiSe_2 , $9.2 \times 10^{-8} \text{ mol cm}^{-2}$, but slightly above the values obtained from materials containing higher amounts of Co (Fig. 4i and S8). These values were consistent with those previously obtained from Ni-based chalcogenide.[55,56].

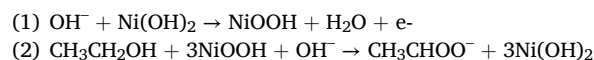
The proton diffusion is generally regarded as a rate-limiting step that controls the $\text{Ni}(\text{OH})_2 \leftrightarrow \text{NiOOH}$ redox reaction in Ni-based electrodes.[57] In the scan rate range 60–100 mV s^{-1} (Fig. 4j), both the anodic and cathodic peak current (i_p) were found to be a linear function of the square root of scan rate ($\nu^{1/2}$), inferring a diffusion-limited redox

reaction within the NiSe_2 and the bimetallic selenides. Thus, according to the Randles–Sevcik equation, we investigated the diffusion coefficient (D) of the redox limiting species within the electrodes using the following equation:[58].

$$I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C \nu^{1/2}$$

where n and C are the electron transfer number (assumed to be 1) and the initial concentration of redox species, respectively. The concentration of $\text{Ni}(\text{II})$ was found to be 3.97 g cm^{-3} , thus we estimated the C value to be $0.043 \text{ mol cm}^{-3}$. [44,55] Based on this equation, the diffusion coefficient of the redox limiting species in the $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ electrode was estimated at $1.2 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, an order of magnitude above that of the other two Ni-Co-based selenide electrodes (Fig. 4i and S8), but well below that of NiSe_2 , $5.0 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$.

The mechanism of the partial ethanol oxidation to acetate involves two main steps: (1) $\text{Ni}(\text{OH})_2$ activated to NiOOH , and (2) the subsequent oxidation of the adsorbed intermediate:[59–62].



The $\text{Ni}(\text{OH})_2$ oxidation to NiOOH is generally considered to be the limiting step.[63] The partial substitution of Ni by Co within the Ni_2Se certainly implies a slight reduction of the amount of surface NiOOH , but much higher EOR current densities were obtained for $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ when compared with NiSe_2 . This could be directly related to a higher surface area, better kinetics of NiOOH formation, and/or more effective ethanol adsorption by the introduction of Co in the NiSe_2 structure.[59].

Fig. 5a displays the CA test for $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ electrode in 1 M KOH + 1 M ethanol at 1.3, 1.4, 1.5, 1.6, and 1.7 V. After reacting for 2000 s, a small portion of the electrolyte was analyzed by IC (see details in the experimental section). As shown in Fig. 5b, the peak at 4.6 min in the IC profile was associated with acetate, which was the only identified product of the ethanol electrooxidation on $\text{Ni}_{0.75}\text{Co}_{0.25}\text{Se}_2$ electrodes. No acetate was detected at 1.3 V, where EOR was not activated on NiOOH . The cumulative acetate concentration in solution was

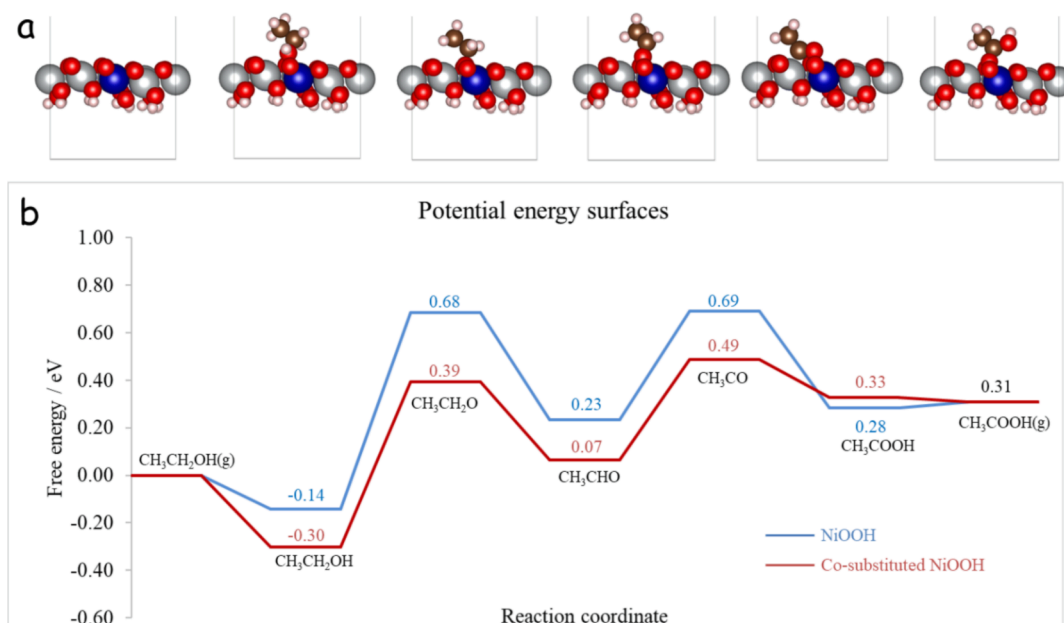


Fig. 6. (a) DFT optimized adsorbed intermediates on the Co-containing NiOOH surface of Ni_{0.75}Co_{0.25}Se₂ electrode, grey ball for Ni, blue for Co, red for O, orange for H, and wine for C. (b) Gibbs free energy diagrams for the ethanol conversion on NiOOH and Co-containing Ni-OOH surfaces. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

quantified at 0.29, 1.08, 2.01, 2.77 mmol L⁻¹, corresponding to 9.2, 33.5, 61.1, and 82.6 μmol acetate produced at 1.4, 1.5, 1.6, and 1.7 V, respectively. If only considering the acetate production at each potential, the acetate concentration was found to be 0.29, 0.79, 0.93, and 0.75 mM, equaling to 9.2, 24.2, 27.7, and 21.4 μmol (Fig. 5c and Table S3). The acetate production increased with the applied potential, up to 1.6 V. Above this voltage, competition with OER decreased the amount of acetate produced (Figure S14).

The ethanol-to-acetate Faradaic efficiency (FE) was calculated using the following equation:

$$FE(\%) = \frac{\text{mol of product} \times n \times F}{\text{total charge passed}} \times 100\%$$

where n is the electron transfer number (assumed to be 4 for the ethanol-to-acetate reaction), and F is the Faradaic constant (96485 C mol⁻¹).

For Ni_{0.75}Co_{0.25}Se₂ electrodes, the lowest ethanol-to-acetate Faradaic efficiency for the ethanol to acetate was achieved at 1.4 V, and it was found to increase above 80% at 1.6 V, and then decrease at higher potentials due to the activation of the competing OER. More quantitatively, a total charge of 6.9, 12.2, 12.9, and 13.4C passed through the electrode at 1.4 V, 1.5 V, 1.6 V and 1.7 V, which translated into a Faradaic efficiency of 51.9%, 76.6%, 82.9% and 61.7%, respectively (Table S3). In the absence of 1 M ethanol, the current generated from OER became more obviously at 1.6 V and higher potentials (Fig. S9a and Table S3).

The long-term stability of the electrocatalyst was tested using CA at 1.5 V. As can be seen in Fig. 5d, almost all the electrodes suffered a rapid decay in current density for the first several minutes. Around 71.3%, 56.4, 90.6%, 90.4, and 64.6% of the initial current densities were lost after 1x10⁴ s operation (Fig. 5e). The activity loss is mainly associated with the accumulation of strongly adsorbed intermediate species poisoning the active surface sites. But changes in the surface chemistry of the electrode, including element rearrangement, surface aggregation of the elements and phase evolution in alkaline media at a high external potential could also play an important role. [64–66].

For the Ni_{0.75}Co_{0.25}Se₂ electrode, a stable current density of 45 mA cm⁻², corresponding to 1.2 A g⁻¹, was sustained over the entire test after the initial rapid decay. The current density decay was well below

that of other non-precious electrocatalysts as noted in Table S2. Besides, since the regeneration of the electrocatalyst is an important merit for the catalytic process, we run two consecutive CA tests for 10⁴ s in 1 M KOH and 1 M ethanol at 1.5 V vs. RHE, replacing the electrolyte in between the two tests. As can be seen in Fig. S10, similar trends of decay and significant regeneration behaviours were observed. Specifically, the current density at 1.5 V was largely improved after replacing the electrolyte and the stability was sustained to around 35 mA cm⁻², slightly lower than that obtained during the first CA measurement. As can be seen in Fig. S11, similar NPs were observed both after long-term EOR and OER CA operation.

IC analysis of the solution after 1x10⁴ s operation (Fig. S12) showed the produced acetate amount to reach 182.3 μmol for the Ni_{0.75}Co_{0.25}Se₂ electrode, well above the values obtained for NiSe₂ (80.2 μmol) and the other Ni-Co selenides (Table S3). The rate of acetate production on the Ni_{0.75}Co_{0.25}Se₂ electrode was 0.34 mmol cm⁻² h⁻¹. In terms of ethanol-to-acetate Faradaic efficiency, NiSe₂ reached 91.3%, and this value decreased with the incorporation of Co (Table S4).

CA at 1.5 V in 1 M KOH showed the contribution of current not associated to EOR to increase with the Co addition, from 1.9% for NiSe₂ and 1.8% for Ni_{0.75}Co_{0.25}Se₂, to values well above 10% for materials containing higher amounts of Co (Fig. S19b and Table S4). Thus the decrease of ethanol-to-acetate Faradaic efficiency with the increase of the Co content was associated with the enhanced OER performance.

The EOR electrocatalytic mechanism and the role of Co in the NiSe₂ electrode were systematically investigated by DFT. Since NiOOH is the active surface for EOR in alkaline solution, we built two slab models, NiOOH, and Co-substituted NiOOH. Fig. S13 and 6a show the adsorbed intermediates on the NiOOH and Co-substituted NiOOH surface, respectively. Fig. 6b compares the corresponding Gibbs free energy diagram. The ethanol molecule adsorption energy was calculated to be -0.14 eV and -0.30 eV on the NiOOH and Co-substituted NiOOH surface, indicating stronger ethanol adsorption in the presence of cobalt. The presence of cobalt decreases the formation energy of the intermediate CH₃CH₂O through a dehydrogenation process, from 0.82 eV for NiOOH, to 0.69 eV for Co-substituted NiOOH. The conversion of CH₃CH₂O to CH₃CHO is energetically downwards for both catalysts, with a free energy change of -0.45 eV for and -0.32 eV for Co-substituted NiOOH. Both catalysts show a similar barrier (0.46 eV for

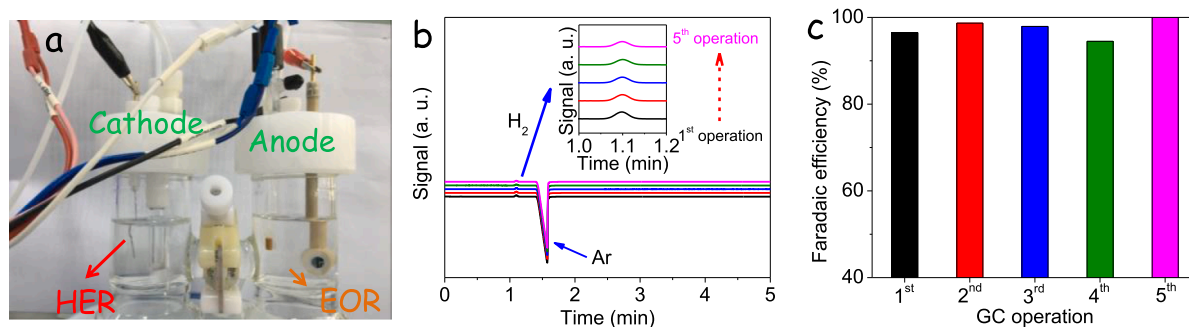


Fig. 7. (a) Setup for the H-type cell with two compartments. (b) GC curves within 1 h GC sampling at the cathode. (c) Calculated Faradaic efficiency for HER.

NiOOH and 0.42 eV for Co-NiOOH) for the third dehydrogenation step, which results in adsorbed CH₃CO. This dehydrogenation process is generally accompanied by the reduction of NiOOH to Ni(OH)₂. Last, adsorbed CH₃CO is released when interacting with OH⁻ ions to form CH₃COOH.

To detect and quantify the gas product generated at the cathode, an H-type cell with two compartments separated by a proton exchange membrane was used (Fig. 7a). The cell contained 1 M KOH and 1 M ethanol in both compartments. At the cathode side, high-purity Ar was used to carry the produced gas to the GC. As can be seen in Fig. 7b, two peaks were located at ca. 1.1 and 1.5 min, which were associated with molecular hydrogen and argon. By comparing with known standard hydrogen concentrations, the calculated Faradaic efficiency was determined to be nearly 100% (Fig. 7c), indicating that only hydrogen was produced on the cathode. In the absence and presence of ethanol in the electrolyte, a total charge of 1.6C and 85.6C passed through the Ni_{0.75}Co_{0.25}Se₂ electrode and the Pt wire, respectively (Table S4). In the presence of ethanol, over 50-fold higher hydrogen was produced during the 10,000 s operation.

4. Conclusion

In summary, we developed a solution-based method to produce Ni_{1-x}Co_xSe₂ NPs with tuned metal ratios. The electrochemical performance of the materials was tested in 1 M KOH and 1 M KOH + 1 M ethanol aqueous electrolytes. CoSe₂ showed enhanced OER activity and NiSe₂ demonstrated a more efficient EOR. The incorporation of small amounts of Co to the NiSe₂ structure resulted in the highest EOR activities. DFT calculations showed that the presence of Co improved ethanol adsorption and decreased the barrier for ethanol dehydrogenation. A current density up to 82.3 mA cm⁻² was achieved for Ni_{0.75}Co_{0.25}Se₂ in 1 M KOH + 1 M ethanol electrolyte at 1.55 V, which is twofold higher than that obtained for NiSe₂. Over 10,000 s testing, the optimized electrocatalyst delivered an average acetate production rate of 0.34 mmol cm⁻² h⁻¹. Additionally, the ethanol-to-acetate faradaic efficiency was determined as 82.3%. This work provides a cost-effective approach to the high Faradaic efficiency electrochemical reforming of ethanol with acetate co-production. This work is also an excellent example for other small molecules oxidation and conversion into valuable chemicals.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2022.135817>.

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