Electrochemical water splitting based on metal oxide composite nanostructures

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Cover page diagram showing the electrochemical water splitting in the presence of metal oxide nanocomposite resulting in the production of hydrogen and oxygen taking place.

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Dedicated to my family

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Norrköping, June 2020

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Abstract

The occurrence of available energy reservoirs is decreasing steeply, therefore we are looking for an alternative and sustainable renewable energy resources. Among them, hydrogen is considered as green fuel with a high density of energy. In nature, hydrogen is not found in a free state and it is most likely present in the compound form for example H_2O . Water covers almost 75% of the earth planet. To produce hydrogen from water, it requires an efficient catalyst. For this purpose, noble materials such as Pt, Ir, and Ru are efficient materials for water splitting. These precious catalysts are rare in nature, very costly, and are restricted from large-scale applications. Therefore, search for a new earth-abundant and nonprecious materials is a hot spot area in the research today. Among the materials, nanomaterials are excellent candidates because of their potential properties for extended applications, particularly in energy systems. The fabrication of nanostructured materials with high specific surface area, fast charge transport, rich catalytic sites, and huge ion transport is the key challenge for turning nonprecious materials into precious catalytic materials. In this thesis, we have investigated nonprecious nanostructured materials and they are found to be efficient for electrochemical water splitting. These nanostructured materials include $\text{MoS}_2\text{-TiO}_2$, MoS_2 , TiO_2 , $\text{MoS}_x\text{@NiO}$, NiO , nickel-iron layered double hydroxide ($\text{NiFeLDH}/\text{Co}_3\text{O}_4$), NiFeLDH , Co_3O_4 , Cu-doped MoS_2 , $\text{Co}_3\text{O}_4\text{-CuO}$, CuO , etc. The composition, morphology, crystalline structure, and phase purities are investigated by a wide range of analytical instruments such as XPS, SEM, HRTEM, and XRD. The production of hydrogen/oxygen from water is obtained either in the acidic or alkaline media. Based on the functional characterization we believe that these newly produced nanostructured materials can be capitalized for the development of water splitting, batteries, and other energy-related devices.

Keywords: Composite metal oxides, hydrothermal method, water splitting, Tafel slope, stability, durability, alkaline media, acidic media

List of papers included:

- i. Advanced electrocatalysts for hydrogen evolution reaction based on core-shell MoS₂/TiO₂ nanostructures in acidic and alkaline media
A. Tahira, Z. H. Ibupoto, R. Mazzaro, S. You, V. Morandi, M. M. Natile, M. Vagin, A. Vomiero, **ACS Appl. Energy Mater.** 2019, 2, 2053-2062
Contribution: I did material synthesis, partial characterization except for HRTEM and XPS and wrote the first draft of the manuscript
- ii. MoS_x@NiO Composite Nanostructures: An advanced nonprecious catalyst for hydrogen evolution reaction in alkaline media
Z. H. Ibupoto, **A. Tahira**, P.Y. Tang, X. Liu, J. R. Morante, M. Fahlman, J. Arbiol, M. Vagin, A. Vomiero, **Adv. Fun. Materials.** 2019, 29, 1807562
Contribution: I did SEM and XRD analysis and critically edited the first draft of the manuscript
- iii. An efficient bifunctional electrocatalyst based on a nickel-iron layered double hydroxide functionalized Co₃O₄ core-shell structure in alkaline media
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Contribution: I performed the preparation of layered double hydroxide onto Co₃O₄ and carried out SEM and XRD characterization. Also, did the water splitting measurements and wrote the first draft of the manuscript
- iv. Advanced Co₃O₄-CuO nano-composite based electrocatalyst for efficient hydrogen evolution reaction in alkaline media
A. Tahira, Z. H. Ibupoto, M. Willander, O. Nur, **Inter. J. Hydr. Energy**, 2019, 44, 26148–26157
Contribution: I synthesized the nanocomposite and carried out the SEM and XRD analysis. The hydrogen evolution reaction was performed by me and wrote the first draft of the manuscript

- v. The chemically reduced CuO–Co₃O₄ composite as a highly efficient electrocatalyst for oxygen evolution reaction in alkaline media

U. Aftab, **A. Tahira**, R. Mazzaro, M. I. Abro, M. M. Baloch, M. Willander, O. Nur, C. Yu, Z. H. Ibupoto, **Catal. Sci. Technol.**, 2019,9, 6274-6284

Contribution: I prepared the composite material prior to the chemical treatment and did XRD analysis. Also, I was involved in the editing of the first draft of the manuscript

- vi. Electronic and structural disorder in Cu-MoS₂ composite nanostructures for efficient hydrogen evolution reaction in acidic and alkaline media

Z. H. Ibupoto, **A. Tahira**, R. Mazzaro, M. M. Natile, M. Vagin, A. Vomiero, **manuscript**, 2020.

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List of papers not included:

1. Facile efficient earth abundant NiO/C composite electrocatalyst for the oxygen evolution reaction
A. Q. Mugheri, **A. Tahira**, U. Aftab, M. I. Abro, S. R. Chaudhry, L. Amaral, Z. H. Ibupoto, **RSC Adv.**, 2019, 9, 5701-5710
2. A practical non-enzymatic urea sensor based on NiCo₂O₄ nanoneedles
S. Amin, **A. Tahira**, A. Solangi, V. Beni, J. R. Morante, X. Liu, M. Falhman, R. Mazzaro, Z. H. Ibupoto, A. Vomiero, **RSC Adv.**, 2019, 9, 14443-14451
3. Efficient Ni-Fe layered double hydroxides/ZnO nanostructures for photochemical water splitting
E. Mustafa, **A. Tahira**, R. E. Adam, Z. H. Ibupoto, S. Elhag, M. Willander, O. Nur
J. Solid-State Chemistry. 2019, 273, 186-191
4. Co₃O₄/ NiO bifunctional electrocatalyst for water splitting
A. Q. Mugheri, **A. Tahira**, U. Aftab, M. I. Abro, S. R. Chaudhry, L. Amaral, Z. H. Ibupoto, **Electrochimica Acta**, 2019, 306, 9-17
5. A sensitive enzyme-free lactic acid sensor based on NiO nanoparticles for practical applications
S. Amin, **A. Tahira**, A. Solangi, R. Mazzaro, Z. H. Ibupoto, A. Vomiero
Anal. Methods, 2019, 11, 3578-3583
6. Efficient photo catalysts based on silver doped ZnO nanorods for the photo degradation of methyl orange
M. A. Bhatti, A. A. Shah, K. F. Almani, **A. Tahira**, S. E. Chalangar, A. D. Chandio, O. Nur, M. Willander, Z. H. Ibupoto, **Ceramics International.**, 2019, 45, 23289-23297
7. An advanced and efficient Co₃O₄/C nanocomposite for the oxygen evolution reaction in alkaline media
A. Q. Mugheri, **A. Tahira**, U. Aftab, M. I. Abro, A. B. Mallah, G. Z. Memon, H. Khan, M. A. Abbasi, I. A. Halepoto, S. R. Chaudhry, Z. H. Ibupoto
RSC Adv., 2019, 9, 34136-34143
8. Facile synthesis of copper doped ZnO nanorods for the efficient photo degradation of methylene blue and methyl orange
A. A. Shah, M. A. Bhatti, **A. Tahira**, A. D. Chandio, I. A. Channa, A. G. Sahito, S. Ebrahim, M. Willander, O. Nur, Z. H. Ibupoto

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9. Efficient tri-metallic oxides $\text{NiCo}_2\text{O}_4/\text{CuO}$ for the oxygen evolution reaction
A. Q. Mugheri, **A. Tahira**, U. Aftab, A. L. Bhatti, N. N. Memon, J.U.R. Memon, M. I. Abro, A. A. Shah, M. Willander, A. A. Hullio, Z. H. Ibupoto
RSC Adv., 2019,9, 42387-42394
10. Functional Nickel Oxide Nanostructures for Ethanol Oxidation in Alkaline Media
S. Amin, **A. Tahira**, A. R. Solangi, R. Mazzaro, Z. H. Ibupoto, A. Fatima, A. Vomiero
Electroanalysis, 2020, 32, 1– 9
11. Facile doping of nickel into Co_3O_4 nanostructures to make them efficient for catalyzing the oxygen evolution reaction
A. L. Bhatti, U. Aftab, **A. Tahira**, M. I. Abro, M. K. samoon, M. H. Aghem, M. A. Bhatti, Z. H. Ibupoto, **RSC Adv.**, 2020, 10, 12962
12. Mixed $\text{CoS}_2@\text{Co}_3\text{O}_4$ composite material: An efficient nonprecious electrocatalyst for hydrogen evolution reaction
U. Aftab, **A. Tahira**, A. H. Samo, M. I. Abro, M. M. Baloch, M. Kumar, Sirajuddin, Z. H. Ibupoto, **Inter. J. Hydr. Energy**, <https://doi.org/10.1016/j.ijhydene.2020.03.131>

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Abbreviations and symbols

AgCl	Silver chloride
B. E	Binding Energy
BET	Brunauer-Emmett-Teller
CE	Counter electrode
Co	Cobalt
Co ₃ O ₄	Cobalt oxide
CoCl ₂ ·6H ₂ O	Cobalt chloride hexahydrate
Cu	Copper
CuO	Copper oxide or Cupric oxide
CuCl ₂ ·2H ₂ O	Copper chloride dihydrate
CV	Cyclic voltammetry
(CH ₂) ₆ N ₄	Hexamethylenetetramine
CO(NH ₂) ₂	Urea
EDS	Energy dispersive x-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
Ev	Electron volt
Fe	Iron
Fe (NO ₃) ₃ ·9H ₂ O	Ferric nitrate nonahydrate
FTO	Fluorine doped tin oxide
GCE	Glassy carbon electrode
H ₂	Hydrogen
H ₂ SO ₄	Sulphuric acid
HCL	Hydrochloric acid
HER	Hydrogen evolution reaction
HRTEM	High-resolution transmission electron microscopy
ICDD	International Center of Diffraction Data
IrO ₂	Iridium Oxide
JCPDS	Joint Committee on Powder Diffraction Standards
KCl	Potassium chloride
KOH	Potassium hydroxide
LSV	Linear sweep voltammetry
M	Molar
MO	Metal Oxide
MoS ₂	Molybdenum disulfide
Mv	Milli volt
mA/cm ²	Milliampere per centimeter Square
mV/s	Milli volt per second
mVdec-1	Milli volt per decay
N ₂	Nitrogen
NaBH ₄	Sodium borohydride
Ni	Nickel

NiO	Nickel oxide
NiFe LDH	Nickel iron layered double hydroxide
NiCo ₂ O ₄	Nickel cobaltite
Ni (OH) ₂	Nickel hydroxide
Ni (NO ₃) ₂ ·6H ₂ O	Nickel nitrate hexahydrate
NRs	Nanorods
NWs	Nanowires
OER	Oxygen evolution reaction
OH ⁻	Hydroxide
O ²⁻	Oxide
Pt	Platinum
RE	Reference electrode
RHE	Reversible hydrogen electrode
RuO ₂	Ruthenium (IV) oxide
SEM	Scanning electron microscopy
SO ₄ ⁻²	Sulphate
SnO ₂	Tin (IV) oxide
STEM	Scanning Transmission Electron Microscopy
TEM	Transmission electron microscopy
TiO ₂	Titanium dioxide
WE	Working electrode
XPS	X-ray photoelectron spectroscopy
XRD	X-ray powder diffraction
λ	wavelength

CHAPTER 1

Background and Motivation

1.1. Available energy resources and alternative strategies

Advancement in the economy in the 21st century is largely dependent on the use of energy for an extended range of applications and at the same time, it creates issues related to the environment because a huge amount of energy is coming from fossil fuels. The fossil fuels include petroleum (36%), coal (27%), and natural gas (23.4%) and they are rich with carbon content. They produce 21.3 billion tons of carbon dioxide (CO₂) per annum when fossil fuels are combusted.¹ CO₂ is among the greenhouse gases and significantly contribute to global warming. The natural reservoirs of these fossil fuels are limited and steeply decrease with the time due to their continuous consumption; therefore scientists/researchers are putting extensive efforts to investigate new alternative and renewable energy reservoirs with zero carbon emission in the environment.

To uplift the standard of society, the key steps are:

- To replace fossil fuels with renewable energy resources.
- To use available energy from the environment.
- To develop devices that would give out low content of carbon into the environment.

The production of neat alternative energy is used by researchers at the large and small scale. On a large scale, nuclear energy, hydroelectric, and solar energy are exploited to produce alternative energy reservoirs. At the small scale, new and emerging technologies are used to design self-powered tools.

1.2. Nanotechnology

Nanotechnology is attributed to the manipulation of matter at molecular, atomic, and supramolecular levels (1 nm to 100 nm). This leads to the development of new technologies with high accuracy and precession using atoms and molecules for the design of macro devices.^{2,3} The concept of nanoscience was first introduced by Richard Feynman an American physicist, “There is plenty of room at the bottom”. He presented this concept at the scientific meeting held at Caltech in 1959. Further, Richard Feynman emphasized that these new products based on nanotechnology will emerge from the combination of Physics, Chemistry and

Biology.⁴ Later, in 1974 Norio Taniguchi described the term ‘Nanotechnology’ in International Congress on Production Engineering, in Tokyo, to discuss the fabrication of semiconducting materials including thin films and ion beam milling at 1nm level. Further, Norio Taniguchi defined the term “Nanotechnology” as division, consolidation, and reshaping of materials into a single molecule or atom.^{5,6} The nanoscience became popular in the 1980s, after the discovery of Gerd Binnig and Heinrich Rohrer on scanning tunneling microscope (STM), and in 1986 they had won a noble prize on this invention.^{7,8} Also, Calvin Quate and Christoph Gerber have invented the atomic force microscope (AFM) which is used to investigate the materials at nano dimensions. Richard Smalley and Robert Curl had found fullerenes (C60) in 1985^{9,10} and Sumio Iijima prepared carbon nanotubes who also made multi-walled carbon nanotubes in 1991.¹¹ The nanostructured materials exhibit unique features such as a high surface area to volume ratio, fast electron communication, charge transport, and excellent catalytic properties, among other unique properties.

1.3. Metal oxide nanostructures

Recently, the research on metal oxides has been going on extensively due to their unique properties and tunable optical bandgap.¹² The chemistry of metal oxides involves ionic bonding between metallic cations and anion of oxide, and it brings them into the category of ionic solids. Metal oxides have filled S-shell configuration; therefore, they are known to be thermally and chemically stable.^{13,14} However, metal oxides have partially filled d-subshells which gives them fascinating properties and further to use them into a broad spectrum of electronic systems. The characteristics of metal oxides are wide range bandgaps,^{15,16} high dielectric constants,¹⁷⁻¹⁹ favorable electronic transitions,^{20,21} good electrical conductivity,^{22,23} optical absorption,^{24,25} electrochromic behavior^{26,27} and improved conductivity.^{28,29} These unique features of metal oxides allow them as materials with potential for an extended range of device applications.

1.4. Electrochemical water splitting

Electrochemical/photochemical water splitting is among the potential methods for the provision of renewable energies such as hydrogen/oxygen production, which can be used in the rechargeable energy devices.³⁰⁻³⁴ Till today, the RuO₂/IrO₂ and Pt are only efficient materials for electrochemical water splitting.³⁵ These noble catalysts are expensive and rarely found in nature therefore, the development of earth-abundant, active, nonprecious, and stable catalysts

for overall water splitting is of prime need and important. Recently, various earth-abundant and low-cost metal oxides such as Mn_3O_4 ,³⁶ NiO ,^{37,38} Co_3O_4 ,³⁹⁻⁴¹ and NiCo_2O_4 ^{42,43} are reported and found as promising catalysts for water splitting. Transition metal oxides are considered among the materials which can be regarded as bi-functional catalysts due to their excellent stability in alkaline media and, they have a wide electrochemical potential range.⁴⁴⁻⁴⁶ They are used for both oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) and are found to be excellent candidates.

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CHAPTER 2

Materials Perspective

Nanostructured materials based on metal oxides are important because of their diverse potential applications including electronics, optoelectronics sensors, and catalysis, etc. Among them, bi-metallic layered double hydroxides especially (NiFeLDH), cobalt oxide (Co_3O_4), nickel oxide (NiO), cupric oxide (CuO), titanium dioxide (TiO_2) and molybdenum disulfide (MoS_2) has been investigated in this research study.

2.1. Cobalt oxide (Co_3O_4)

Cobalt oxide as cobalt (II, III) oxide is one of the inorganic compounds having a chemical formula of Co_3O_4 . It is among the potential forms of cobalt oxide; in color, it is blackish and carries a mixture of oxidation states in its structure. Co_3O_4 is represented as $\text{CoIICoIII}_2\text{O}_4$ and sometimes as $\text{CoO} \cdot \text{Co}_2\text{O}_3$ ³ in the spinel structure of Co_3O_4 . The Co^{2+} ions are at tetrahedral positions and Co^{3+} are at octahedral positions and they give a cubic structure with a packing of lattices of oxide anions.¹

Cobalt (II) oxide (CoO) transform into Co_3O_4 upon heating in air to a temperature from 600-700°C.¹ However, CoO is stable above 900°C^{1,2} and it can be represented by the following chemical reaction:

The cobalt oxide is considered a blue coloring agent for pottery enamel and glass.³ Cobalt (II, III) oxide is found as strong electrode stuff in lithium-ion batteries and water splitting especially in nanostructured form.

2.2. Nickel iron layered double hydroxide (NiFeLDH)

The LDH is a class of layered anionic substances and has received significant attention because of their favorable ion-exchange capability, high specific surface area and soft structures.⁴⁻⁶ However, the low conductivity of LDH is a barrier for electron transfer and limits the rate of mass diffusion at the time of the redox process. Besides the low conductivity of the LDH, they also suffer from agglomeration that gives them a low energy density and poor cycling stability at the time of charge/discharge process. It is a well-established concept that the electrochemical activity of LDH can be enhanced efficiently when they are coupled with carbon materials. The

use of carbon materials effectively reduces the agglomeration of LDH, enlarge the specific surface area and improves electrical conductivity of LDH.^{5,7,8} NiFeLDH material has high crystallinity and exhibits hexagonal shapes and is known to be an excellent candidate for energy storage devices⁹ and it has been studied for water splitting or water oxidation.¹⁰

2.3. Nickel oxide (NiO)

Nickel (II) oxide is an inorganic compound with the chemical formula NiO.¹¹ It is known as basic metal oxide and a million kilograms of NiO are produced with different quality per year, particularly in the form of nickel alloys.¹² NiO is produced by several methods. For example, nickel powder reaction with oxygen at 400°C yields NiO. Commercially, heating a mixture of nickel powder and water at 1000°C gives a green-colored NiO. The facile approach to produce NiO involves pyrolysis of nickel (II) compounds including hydroxide, nitrate, and carbonate and they give a green powder of NiO.¹¹ Also, the preparation of NiO from the elements with thermal treatment of metal in the presence of oxygen in the air can give grey to black powders in a nonstoichiometric form.¹¹

NiO exhibits a cubic crystal structure like NaCl in which octahedral sites are occupied by both Ni²⁺ and O²⁻. Often, NiO is found with a nonstoichiometric ratio in which Ni:O ratio differs from 1:1 and this is confirmed by the color change. A green powder of NiO is a stoichiometric compound however, the black color indicates the nonstoichiometric NiO. Pure NiO as the chemical-grade is used in special applications and metallurgical grade is used in the preparation of alloys. NiO is also used in nickel-iron batteries and as a component of fuel cells. NiO is investigated as a hydrogenation catalyst and it is used as an electrocatalyst for water oxidation.

2.4. Cupric oxide (CuO)

Cupric (II) oxide is among the first-row transition metal oxides with chemical formula CuO and in the mineral form, it is called tenorite.¹³ On a large scale, it is produced through pyrometallurgy by extracting copper from its ores. The ores interact with an aqueous mixture of ammonium carbonate, ammonia, and oxygen to produce copper (I) and copper (II) amine complexes, and further, these complexes are thermally decomposed into CuO in the presence of steam. CuO can be prepared by heating copper in the air at a temperature range from 300-800°C. Also, copper (II) oxide in pure form is synthesized by thermal treatment of copper (II) nitrate, copper (II) hydroxide, or alkaline copper (II) carbonate.¹⁴ The crystallography of CuO gives a monoclinic phase in which the copper atom is coordinated via 4 oxygen atoms and

showing a square planar structure.¹⁵ CuO is used in the synthesis of copper salts. CuO is used as a pigment in ceramics and it gives a blue, red, and green glazes. CuO is used as an electrode of the Edison-Lalande cell.^{16,17}

2.5. Titanium dioxide (TiO₂)

Titanium dioxide is named titanium (IV) oxide and in nature, it is found oxide of titanium with chemical structure TiO₂. It is known as titanium white when used as a pigment. As a mineral, it is found either in rutile or anatase. TiO₂ is used in diverse applications such as paint, sunscreen, and food coloring. Titanium dioxide is used as photocatalyst particularly in anatase form it has significant activity in the UV region.^{18,19}

2.6. Molybdenum disulfide (MoS₂)

Molybdenum disulfide (or moly) is a layered inorganic compound consisting of molybdenum and sulfur in its structure with chemical formula MoS₂. It is one of the members of the metal chalcogenide family. It appears as a silver blackish solid and found as the mineral molybdenite.²⁰ MoS₂ is chemically inactive and remains unaltered when treated with dilute acids and oxygen. MoS₂ has the same features as that of graphite and used as a lubricant due to its low friction property. MoS₂ in bulk form is diamagnetic with indirect bandgap semiconducting material like silicon with an optical bandgap of 1.23 eV.²¹

MoS₂ has a layered structure in all forms wherein molybdenum atoms are sandwiched by planes of sulfide ions. In bulk form, MoS₂ has a stacked monolayer structure which exists via weak Van der Waals forces. In crystalline form, MoS₂ is found in two phases such as 2H-MoS₂ and 3R-MoS₂, herein H indicates the hexagonal and R as rhombohedral symmetry.²² Another metastable crystalline phase of MoS₂ is known as 1T-MoS₂ which is obtained via intercalating 2H-MoS₂ with alkali metals.²³ This form of MoS₂ has tetragonal symmetry and it exhibits metallic properties. 1T-MoS₂ can be transformed into 2H-phase via microwave radiation.²⁴ MoS₂ is used in a wide range of electronic and optoelectronic applications. It is also used in catalysis. MoS₂ is known as an excellent hydrogen evolution reaction catalyst.

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CHAPTER 3

Material Synthesis

In this chapter, we will provide detailed processes related to material synthesis. The synthesis of, TiO_2 , MoS_2 , $\text{MoS}_2\text{-TiO}_2$, NiO , $\text{MoS}_2\text{-NiO}$, nickel-iron layered double hydroxide (NiFeLDH) deposited on Co_3O_4 , Co_3O_4 , $\text{Co}_3\text{O}_4\text{-CuO}$ and chemically reduced $\text{Co}_3\text{O}_4\text{-CuO}$ composites. The methodology for the preparation is presented according to our reported works and it reveals the reproducibility of our growth process used for the synthesis of various nanostructured materials. Both the deposition on substrate and powder collection using filter paper were used for the synthesized nanostructured materials for further characterizations.

3.1. Preparation of $\text{MoS}_2\text{-TiO}_2$ core-shell nanostructures

The TiO_2 , MoS_2 and $\text{MoS}_2\text{-TiO}_2$ nanostructured materials were grown on conducting glass substrate via hydrothermal method.¹ The precursors were used without further treatment. Before the deposition of materials on FTO, it was cleaned with acetone in an ultrasonic bath and washed with deionized water followed by ethanol. Then the FTO substrates were dried. First, FTO was covered with the TiO_2 seed layer through the drop-casting method, then seed layer coated FTO substrates were annealed at 500°C in the air for 20 minutes. The TiO_2 seed particles were prepared from titanium butoxide and absolute ethanol. The growth solution consisting of 1g of titanium butoxide TTIP, 6 mL n-butanone, and 6 mL 37% HCl. The seed layer coated substrate was kept in the bottom of a Teflon vessel then the solution was poured into a Teflon vessel, the autoclave thermally treated at 180°C for 40 - 60 minutes. The core-shell $\text{MoS}_2\text{-TiO}_2$ nanostructures were carried by the hydrothermal method. The precursor solution of MoS_2 was prepared by dissolving 0.17g of ammonium phosphomolybdate hydrate and 0.275g of L-cysteine in 50 mL. The growth of MoS_2 on TiO_2 nanorods was carried out in autoclave at 200°C for 24 hours. For comparison, pure MoS_2 nanostructures were also grown on conducting substrate.

Fig.3.1 (a) shows the nanorods like morphology of pristine TiO_2 , and core-shell structure of $\text{MoS}_2\text{-TiO}_2$ composite **Fig.3.1 (b)**. The nanorods are few microns long with a diameter of 50-150 nm. It has been reported that rich active edges of MoS_2 are responsible for the superior HER activity. In this study, MoS_2 was decorated on TiO_2 nanorods and we believe that it exhibits a rich number of catalytic sites to facilitate the HER.¹

Fig. 3.1. SEM images (a) TiO_2 nanorods, (b) MoS_2 - TiO_2 core-shell structure. With a scale bar 200 nm.¹

3.2. Synthesis of MoS_x -NiO nanocomposite

The synthesis of the MoS_x -NiO nanocomposite was prepared in three steps following the hydrothermal method.² First, NiO nanomaterial was prepared by two steps process. In the first step, nickel hydroxide nanostructures were obtained. For this purpose, a precursor solution was made with 2.37g of nickel chloride hexahydrate and 1.41g of hexamethylenetetramine, then the precursor solution was covered and kept at 95°C for 5 hours. Afterward, nickel hydroxide was collected by filtration. The second step involves the transformation of the hydroxide phase into the oxide via heating at 450°C for 3 hrs. In the third step, MoS_x nanostructures were deposited on NiO nanostructures. For this step, 0.3g of NiO was kept in a precursor solution of MoS_x containing 0.175g ammonium phosphomolybdate hydrate and 0.275g of L-cysteine, then the mixture was transferred into the hydrothermal autoclave and the reaction was carried out at 200°C for 24 hrs. Finally, a composite nanostructure was obtained.

Fig.3.2 (a) indicates a porous morphology of NiO. The loading of the MoS_x layer on NiO, it gives a composite nanostructure with porosity features and consisting of nanoparticles **Fig.3.2 (b)**. XRD study has indicated a cubic phase of NiO and the results are very much compatible with reference card no. (96-101-0382) **Fig.3.2 (c)**. However, after the deposition of MoS_x on NiO, the reflection of the cubic phase of NiS is found fully agreed with reference card no. (96-591-0138) **Fig. 3.2 (d)**. Also, the composite carries reflection peaks of cubic NiO.²

Fig. 3.2. SEM images (a) NiO bare (b) composite with MoS_x (c) XRD diffractograms pure NiO (d) MoS_x@NiO composite (e) XPS S2p spectra (f) S2s and Mo3d spectra MoS_x@NiO composite. In (e, f) the experimental spectra with dots, the fitting curves with dashed and solid lines.²

3.3. Synthesis of hybrid nickel iron layered double hydroxide/Co₃O₄ material

The NiFeLDH/Co₃O₄ hybrid was produced by wet chemical method and the electrodeposition.³ The FTO glass substrates were dipped into methanol and cleaned in an ultrasonic bath for 30 minutes. The seed particles of cobalt oxide were prepared by using 0.1M cobalt chloride hexahydrate and 0.1M KOH in ethanol. Spin coating was used to deposit seed nanoparticles on cleaned FTO substrates and annealed at 130°C for 20 minutes. The annealing is carried for the seed particles to increase the adherence of them on the FTO substrate. The growth mixture was obtained by dissolving 0.1M cobalt chloride hexahydrate and 0.1M urea. Afterward, the seed layer deposited FTO substrates were kept in the solution and covered by aluminum foil. The

heating at 98°C for 6 hours was provided to the growth solution. Further, these hydroxide nanostructures of cobalt were thermally decomposed into cobalt oxide at 500°C for 4 hours. Then cobalt oxide nanostructures were coated with nickel-iron layered double hydroxide (NiFeLDH) using the electrodeposition technique. For this purpose, a precursor solution was made by dissolving nickel nitrate hexahydrate and ferric nitrate nonahydrate. The NiFeLDH deposition on Co₃O₄ was produced at -1.0 volts for 10 minutes.

A schematic diagram is shown in **Fig.3.3 (A)** which explains the synergy produced between NiFeLDH, and cobalt oxide. The SEM images of pristine NiFeLDH, cobalt oxide and NiFeLDH decorated cobalt oxide nanowires are depicted in **Fig.3.3**. The pristine NiFeLDH exhibits porous morphology consisting of a few hundred nm later sides and they are interconnected as shown in **Fig.3.3 (a)**. The pristine cobalt oxide possesses nanowires like morphology which is resulted due to the self-assembly of nanoparticles as shown in **Fig.3.3 (b)**. The cobalt oxide nanowires are few microns in length with a diameter of 50 to 100 nm. After the deposition of the NiFeLDH on cobalt oxide nanowires which gives complete coverage of nanowires and resulting in core-shell nanostructures as shown in **Fig.3.3 (c-d)**. The hybrid structure of cobalt oxide is associated with interconnected with nanosheets of 150 to 300 nm in thickness.

(A)

Fig. 3.3. (A) The scheme shows synergetic effect SEM Images, (a) bare NiFeLDH, (b) bare Co_3O_4 , (c, d) NiFeLDH/ Co_3O_4 core-shell structure.³

3.4. Synthesis of Co_3O_4 -CuO nanocomposite

The Co_3O_4 -CuO nanocomposite was prepared by wet chemical method.⁴ The synthesis involved 2.37g of cobalt chloride hexahydrate, 1.20g of copper chloride dihydrate, and 0.6g of urea. Before the deposition of the Co_3O_4 -CuO nanocomposite on the FTO substrate, it was cleaned in acetone using an ultrasonic bath and washed with deionized water. Then a colloidal solution of cobalt chloride was coated on FTO using the dip-coating technique. After the gentle dip-coating on FTO, it was heated at 130°C for 25 minutes to bind the seed particle firmly

attached to the FTO substrate. After the coating of seed particles on FTO, it was vertically dipped into the precursor with seed coated surface towards precursor solution, then the precursor containing beaker was tightly sealed with aluminum foil and were left in the electric oven at 95°C for 5 hrs. Then the hydroxide nanocomposite was thermally treated at 500°C for 4 hours to transform it into an oxide phase. At the same time, a nano powder was collected from the bottom of the beaker, by using the same annealing, the hydroxide was transformed into an oxide phase. A similar approach was used to produce Co_3O_4 nanostructures in the absence of copper salt in the precursor solution. The bare CuO was obtained by dissolving the copper chloride and urea. Seed coating was carried out on the cleaned FTO substrate and it was kept vertically in the growth solution at 90°C for 5 hours. After the growth duration, a black layer of nanostructured material on FTO was observed. At the same time, the nano powder was collected from the bottom of the beaker for further experiments.

The SEM was employed to study structural information of various materials. The pristine CuO exhibited a leaf-like structure as shown in **Fig.3.4 (a, b)**. Each leaf has a thickness of several hundred and they are homogenous on the substrate. A pristine cobalt oxide carries a nanowire morphology with an average diameter of 200 nm to 500 nm and they are randomly oriented on the substrate as shown in **Fig.3.4 (c, d)**. The composite $\text{Co}_3\text{O}_4\text{-CuO}$ exhibits nanowire like shape, their top surface is thinner and sharp due to the addition of copper chloride during the cobalt oxide growth. Each structure of the composite is a few microns in length with an average diameter of 100-300 nm **Fig.3.4 (e, f)**. An addition of copper into cobalt oxide increased its conductivity which speeds up the HER kinetics.

Fig. 3.4. SEM images (a, b) bare CuO, (c, d) bare Co₃O₄, (e, f) hybrid Co₃O₄-CuO.⁴

3.5. Synthesis of chemically reduced CuO-Co₃O₄ composite

The preparation of CuO-Co₃O₄ composite was carried by using the wet chemical method and chemical reduction.⁵ The synthesis involved 2.37g of cobalt chloride hexahydrate, 0.6g urea, and 1.18g of copper chloride. Then growth solution containing beaker was covered with aluminum foil and kept at 95°C for 6 hours in a preheated electric oven. The pink hydroxide nanostructures were thermally decomposed into the oxide phase at 500°C for 5 hours in the air. It is a well-established concept that the cobalt oxide has poor electrical conductivity therefore, it is considered as inefficient OER catalyst. To improve the conductance of the cobalt oxide, we added an impurity of copper chloride into the precursor solution of cobalt oxide which increased the electrical conductivity of cobalt oxide but has boosted water oxidation. Additionally, the copper chloride did not change the shape features of the nanostructured material. This method was repeated for the synthesis of bare cobalt oxide and CuO. The Co₃O₄-CuO nanocomposite was chemically reduced in the presence of 0.2M NaBH₄ as a reducing

reactant and the chemical reduction of this mixed metal oxide nanostructures was done in a test tube. First, a certain volume of 0.2M NaBH_4 was introduced into a test tube then the nanocomposite was added into it, a vigorous exothermic reaction has then taken place. After a while, the nanoparticles started to settle down at the bottom of the tube. Then the reduced nanoparticles were obtained through centrifugation and it was washed by deionized water. The chemically reduced samples were dried in air and were ready to use for further experiments. The morphology of pristine cobalt oxide, CuO , $\text{CuO-Co}_3\text{O}_4$ and chemically reduced $\text{CuO-Co}_3\text{O}_4$ is shown in **Fig.3.5**. The pristine cobalt oxide exhibits platelets like structure and consisting of nanoparticles as shown in **Fig.3.5 (a)** and they are few microns in length. **Fig.3.5 (b)** shows a leaf-like structure of pristine CuO . The pristine $\text{CuO-Co}_3\text{O}_4$ possesses a rough surface with a flower-like shape as depicted in **Fig.3.5 (c)**. However, the chemically reduced $\text{CuO-Co}_3\text{O}_4$ composite has 2D nanosheets covering the flower-like structure **Fig.3.5 (d)**.

Fig. 3.5. SEM images, (a) Co_3O_4 , (b) CuO , (c) pristine $\text{CuO-Co}_3\text{O}_4$ (d) chemically reduced $\text{CuO-Co}_3\text{O}_4$ composite.⁵

3.6. Preparation of pristine MoS₂ and Cu-induced MoS₂ electrocatalysts.

The preparation of MoS₂ material in pure form was done by using the hydrothermal method.⁶ The precursor solution consisting of 0.175g of ammonium molybdenum hydrate and 0.275g of L-cysteine. The growth was done in stainless steel autoclave at 200°C for 20 hrs. A similar approach was used to produce Cu-induced MoS₂ nanostructures using a different 30%, 46%, and 56 % Cu using copper chloride dihydrate. Typical SEM images for pristine MoS₂ and Cu-induced MoS₂ nanostructures using different 30%, 46%, and 56 % Cu are enclosed in **Fig.3.6**.

Fig. 3.6. SEM images (a) bare MoS₂, (b) 30% Cu-doped MoS₂, (c) 46% Cu-doped MoS₂, (d) 56% Cu-doped MoS₂ at different magnifications.⁶

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CHAPTER 4

Analytical Techniques for the Characterization of Nanostructured Materials

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The material characterization for the understanding of morphology, crystalline structure, chemical constituents, and electrochemical properties by various analytical techniques was the main objective of this study. These techniques were successfully applied to understand the electrochemical processes based on the size and shape of nanostructured materials. For this reason, we used scanning electron microscope (SEM), x-ray diffraction (XRD), transmission electron microscope (TEM), Raman Spectroscopy, x-ray photoelectron spectroscopy (XPS), and electrochemical techniques (CV, LSV, and EIS). The working principle of these techniques is briefly described as follow:

4.1 Powder X-ray diffraction (XRD)

Generally, a wavelength associated with the x-rays is in the range of ($\lambda = 0.15406$) nm which is in between ultraviolet and gamma rays. XRD is considered a fundamental technique to investigate the phase and purity of nanostructured materials and it is known as nondestructive technique. Additionally, XRD gives information about the unit cell, lattice constants, and physical properties of the obtained nanostructured materials. It is believed about the solid materials that they are almost more the 90% crystalline.¹ Each material has its crystal structure which can be identified by the XRD and they are regarded as the “fingerprint” of that material. Diffraction patterns are resulted due to x-ray beam incident on the crystal planes which are used to identify the composition and phase of the material. The diffraction patterns carry information about the size of the crystal, the symmetry of unit cell, stress, strain, and preferred crystal growth direction, etc. Diffraction patterns are produced as follows: The x-ray beam is of wavelength λ interacts with the solid material at an angle θ , and the wavelength of the reflected radiation is determined via Bragg’s equation (i.e. $n \lambda = 2d \sin\theta$). Herein, n indicates the number of reflections, and d is called the interplanar distance between the crystal planes. The value of d -planes is constant for all materials. The manipulation of different parameters such as the geometry of x-rays, the direction of detector, and crystal lead to the provision of information about the orientation of crystal lattices.^{2,3} In this thesis, we used an Empryean instrument, PANalytical PIXcel3D, with Cu K α x-ray source in a Bragg Brentano geometry technique.

4.2. Scanning electron microscope (SEM)

SEM was utilized to know the shapes of nanostructured materials presented in this thesis. The SEM gives information about the quality, morphology, diameter, length, and orientation of the prepared nanostructured materials. SEM uses a beam of electrons to make an image of the material. The electron beam passes by electromagnetic lenses which interact with the material. The interaction of an electron beam does not destroy the surface of the material. The detector provides the secondary electrons taken out from the material and transforms it into a signal. then the signal is displayed at screen.⁴ SEM measures the image in the range of few nanometers with a magnification of 20X- 30000X and a spatial resolution of 50-100nm.^{5,6} The accelerating voltage of electrons is in the range of 5-20 KV and detailed information can be found elsewhere.⁷ The morphology of all the nanostructured materials presented in this thesis is characterized by SEM (FEI Magellan HR-SEM model) running at 15 kV.

4.3. Energy-dispersive spectroscopy (EDS)

EDS is a common technique to identify the chemical constituents in the material especially the presence of elements in a sample. For this purpose, we also used energy dispersive spectroscopy equipped with SEM, and the spectra were collected at different spots of our nanostructured materials. In a typical experimental setup, EDS consisting four basic units, namely, electron beam or x-ray beam), an excitation source (x-ray detector, a pulse processor, and an analyzer. The function of the detector is to transfer energy into a potential signal, then it is transmitted to the pulse processor which gives a signal and then passes them to the analyzer for display and analysis.

4.4. Raman spectroscopy

Raman Spectroscopy developed by the Indian Physicist C.V. Raman. It is a spectroscopic tool to identify the vibrational modes of molecules in general and it is also capable to measure the rotational and low-frequency transit systems.¹ Raman is widely used in Chemistry to elucidate the structural information for the identification of molecules. Raman spectroscopy depends on the inelastic scattering of photons, thus called Raman scattering. The use of single-wavelength light such as laser in near-ultraviolet, visible, or near-infrared is utilized, even x-ray can be involved. The interaction of laser light related to excitations which result in the variation of energy of laser photons. The change in the energy shows the information related to the vibrational modes in each system. In Raman spectroscopy, a material is excited with laser light,

the electromagnetic energy is captured with the lens and sent to the monochromator. The elastic scattering corresponded to the Rayleigh scattering is filtered out via a notch filter is spread on the detector. We used a 50× objective under 532 nm laser excitation and laser power was adjusted to 0.2 mW.¹³

4.5. Transmission electron microscope (TEM)

TEM is among the family member of SEM which involves the electron beam for recording the sample image. TEM gives information at the atomic level and utilized for the characterization of nanostructured compounds. The process for the collection of information about the sample is like that of an optical microscope but in TEM a highly energetic electron beam is used with an accelerating voltage of approximately 200 keV. TEM is a versatile technique to get information about the chemical composition of the sample,⁸ surface information like crystal structure, and image up to a few nm just by adjusting the operational mode. TEM is superior to SEM in terms of multi-direction information about the sample such as high magnification resolution, but it has certain drawbacks/limitations which require attention. Few of them are summarized here:

- It is time taken technique particularly sample preparation requires a lot of time
- It is a destructive technique i.e. it damages the sample
- It provides only local information i.e. information about the selected spot of the sample
- It is a bit difficult to operate when compared to the SEM

In this research work, we used a copper grid for the preparation of samples to analyze through the TEM. We used TEM (FEI Tecnai G2 TF20 UT) gunrunning at 200 keV at a resolution of 1.9Å.

4.6. X-ray photoelectron spectroscopy (XPS)

XPS is a surface-sensitive technique and extensively employed for the determination of the composition. The working principle of XPS is depending on the photo-ionization effect^{9, 10} and it can be described as when the sample is exposed to the x-ray beam, the electrons of atoms at the surface absorbs. Consequently, if the energy of x-rays carries enough energy then the electrons are taken out from the atom having kinetic energy as a photoelectron. The relationship between photon energy and kinetic energy is built as follows:

$$EK = h\nu - E_b$$

Here where EK is the kinetic energy, E_b is the binding energy, and $h\nu$ is the X-ray photon energy. In this research thesis, all the XPS testing was done on a Scienta® ESCA200 in a well vacuum (UHV) and pressure of 10^{-10} mbar. The experimental chamber was set by Al ($K\alpha$) X-ray source for photons (i.e. $h\nu = 1486.6$ eV). The recorded binding energies are reported with the fermi level.

4.7. Electrochemical techniques

All the water splitting testing was performed on a VERSASTAT analytical potentiostat. A three-electrode cell was used. For making a working electrode a catalyst ink was made by mixing 10mg of catalyst in 2 mL deionized water and 50 μ L of 5% Nafion and sonicated 15 minutes to achieve a well-dispersed mixture. Then nanostructured material of 10 μ L was deposited on a 3 mm diameter glassy carbon electrode and used as a working electrode. For the working electrodes fabricated on the FTO substrate, an in-situ growth of nanostructured material was carried out and used them directly without the coating of the Nafion membrane. A silver-silver chloride (Ag/AgCl) as a reference electrode and a platinum wire as a counter electrode. Before water splitting measurements with linear sweep voltammetry (LSV) technique, several cyclic voltammetry (CV) runs were performed at 5 mV. Electrochemical impedance spectroscopy (EIS) was done for the different frequency ranges and the onset potential of OER/HER and certain sinusoidal potential. The durability was monitored either by the chronopotentiometry or chronoamperometry techniques. The iR drop was calculated according to reported methods.^{11,12} All the potentials were reported against the reversible hydrogen electrode (RHE) via the Nernst equation as described below:¹³

$$E_{RHE} = E_{Ag/AgCl} + 0.059 \text{ pH} + E_o \text{ Ag/AgCl.} \quad (1)$$

4.8. References

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CHAPTER 5

Results and Discussion

Herein, we provide some produced results which are then discussed briefly. These results are from the papers which we are defending in this thesis. They are mostly about the composite materials used for water splitting. One of the works is about the fundamental understanding of catalyst design by tailoring with the different precursors and their role in catalytic activity.

5.1. Advanced Electrocatalysts for Hydrogen Evolution Reaction Based on Core-Shell MoS₂/TiO₂ Nanostructures in Acidic and Alkaline media

(Paper I)

In this paper, we produced a MoS₂/TiO₂ core-shell structure on the FTO conducting substrate through the wet chemical approach and used for efficient hydrogen evolution reaction.¹ XRD study has shown the rutile phase of TiO₂ nanorods (JCPDS card no 96-900-9084). The intense peak at 36.1 2theta (deg) [101 orientation] as shown in **Fig. 5.1** is the preferred direction for the growth TiO₂ nanorods (as revealed by TEM). The rutile phase of TiO₂ exists even after the coating of the MoS₂ layer. XRD study showed that no crystalline phase of MoS₂ was detected it is most like amorphous as shown in **Fig.5.1 (a)**. Raman analysis confirms the uniform distribution of TiO₂ nanorods on FTO substrate and the distinctive bands at 240, 440, and 607 cm⁻¹ fully agreed with Titania phase **Fig.5.1 (b)** same as that in XRD analysis. The MoS₂-TiO₂ and pristine MoS₂ samples have noisy Raman bands at 408 cm⁻¹ and it is attributed to the molybdenite. It is assigned to a relatively poor crystalline phase of MoS₂ as confirmed by the XRD study. Further via irreversible laser inducted crystallized was found in MoS₂-TiO₂ composite as the Raman bands height for rutile and molybdenite together were enhanced with increasing laser power.

Fig. 5.1. (a) The XRD spectra bare TiO_2 nanorods and $\text{TiO}_2/\text{MoS}_2$ composite **(b)** Raman spectra TiO_2 , $\text{TiO}_2/\text{MoS}_2$ and MoS_2 materials. Black stars (*) and blue circles (o) refer to Raman peaks for rutile and molybdenite, respectively.¹

Fig.5.2 displays the HRTEM analysis of the MoS_2 - TiO_2 core-shell system. It gives an elongated single crystal structure having a diameter between 200-300 nm and length of 1-4 microns **Fig.5.2 (a)**. The crystalline system agrees with the rutile phase **Fig.5.2 (b)** and the surface of nanorods is completely decorated with continuous later semi-crystalline material. Few 0.61 nm fringes could be identified in **Fig.5.2 (c)** and they are indexed to the (002) patterns of the MoS_2 lattice. The fringes are broader because of the small crystalline features of the MoS_2 structure. Both the STEM results and the EDS mapping at the interface altogether show that the nanorods are surrounded by MoS_2 **Fig.5.2 (d)**. The obtained results of the TEM fully satisfy, Raman, SEM, and XRD analysis.

Fig. 5.2. (a) TEM image for MoS₂ deposited TiO₂ nanorod and Selected Area Diffraction done on the similar nanorod showing a single diffraction pattern (Rutile (1,2,1) Zone Axis), (b) HR-TEM image for the core of MoS₂ deposited on TiO₂ nanorod: inset displaying FFT image, (c) HR-TEM image at the interface between TiO₂ nanorods and MoS₂, showing key aspects of Rutile and Molybdenite crystal systems. (d) STEM-EDS composition image and (inset) distribution of Ti and Mo. Scale bar in (c) and (d) equal to 20 nm.¹

Based on the structural and compositional analysis the core-shell structure may have rich catalytic centers for MoS₂ it could reduce the Tafel slope, overpotential, and increase the exchange current density. To investigate the HER performance of different catalysts, electrolysis of water was carried out in 0.5M H₂SO₄ and 1M KOH electrolytes using three electrode configurations. To stop the resistance of the FTO, the materials were removed, and a catalyst ink was prepared and deposited on a glassy carbon electrode (GCE) and a superior HER activity is demonstrated. **Fig.5.3 (a)** represents the LSV curves of different catalysts at the acidic conditions. The MoS₂/TiO₂ composite shows a small overpotential (approximately 350 mV) compared to the pure MoS₂ and TiO₂. The experimental potentials are transformed after iR drop into a reversible hydrogen electrode (RHE). The GCE seems active for HER at the higher potential in 1M KOH, MoS₂/TiO₂ composite shows water catalysis slightly at higher

potential as shown in **Fig.5.3 (c)**. Still, MoS₂/TiO₂ composite has a smaller overpotential than the pristine MoS₂ and TiO₂. The HER kinetics is governed by the Tafel slope and it is calculated from the linear part of LSV curves **Fig.5.3 (c)**. The Tafel value is measured according to the Tafel equation as described below:

$$\eta = a + b \log j$$

Here a is a constant, b as Tafel value, and j as current density.

In acidic conditions, a Tafel value 48 mVdec⁻¹ found for the MoS₂-TiO₂ core-shell structure and it is smaller than many nonprecious HER catalysts reported recently ^{34,35} as shown in **Fig.5.3 (b)**.

Three steps participate in HER process when performed in an acidic environment.^{2,3,4,5} The first step is the elementary step and known as the Volmer step, the second step is desorption which Heyrovsky, and the third step is Tafel reaction. Tafel value gives information about the rate-determining step involved in the HER process. Pt-based materials exhibit Volmer Tafel kinetics steps 1 and 3, while step 2 is known as a controlled step relatively at low overpotential as supported by the Tafel slope of 30 mVdec⁻¹.^{2,6} MoS₂-TiO₂ core-shell structure has Tafel value 48 mVdec⁻¹ which confirms that it obeys the Heyrovsky step. The Tafel value 32 mVdec⁻¹ in the case of Pt/C shows the Volmer step and the rate of reaction controlled by the reunion of hydrogen atoms on the surface of the catalyst. In case of alkaline conditions, the Tafel slopes were estimated to be 40, and 60 mVdec⁻¹ for Pt/C and MoS₂/TiO₂, respectively, as shown in **Fig.5.3 (d)**. The HER kinetics is followed by the Heyrovsky step in which the desorption is a key rate-determining step. The catalytic activity in terms of Tafel slopes of the MoS₂/TiO₂ hybrid materials in acidic conditions is better than the recently reported catalysts MoS₂⁶, WS₂⁷, WS₂(_{1-x})Se_{2x}⁸, and transition metal sulfides, e.g. CoSe₂⁹, NiSe₂¹⁰, and CoS₂^{11,12}, revealing an excellent HER activity.

Fig. 5.3. (a) LSV curves for various materials at the scan rate of 5 mV/s in 0.5M H₂SO₄ purged with N₂ gas, (b) polarization curves for various materials in 1M KOH purged with N₂ gas, (c) Tafel plots in 0.5M H₂SO₄, (d) Tafel plots in 1M KOH.¹

5.2. MoS_x@NiO composite nanostructures: an advanced nonprecious catalyst for hydrogen evolution reaction in alkaline media

(Paper II)

In this research work, we produced a MoS_x@NiO composite by using the hydrothermal method and it was used for HER in basic conditions.¹³ The crystalline structure, morphology, and chemical composition were also investigated through high angle annular dark field (HAADF), scanning transmission electron microscopy (STEM) coupled with electron energy loss spectroscopy and HR-TEM as shown in **Fig.5.4 (a-d)**. The pristine NiO is mainly consisting of Ni and O. The HRTEM and FFT spectrum show that nanoplates exhibit cubic NiO phase, [FM3-M]-Space group 225, with lattice parameters of $a = b = c = 0.4179$ nm, and $\alpha = \beta = \gamma = 90^\circ$ as seen along the $[110]$ direction. The composite shows at the interface through Field Fourier transmission (FFT) image that it exhibits hexagonal phase of MoS₂, [P63/MMC]-Space group 194, with lattice parameters of $a = b = 0.3165$ nm, $c = 1.2295$ nm, and $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ as seen along the $[1-21-3]$ direction.¹³ The HRTEM information is fully supported by XRD analysis.

Fig. 5.4. (a) EELS composition analysis found from the red rectangle part of the ADF-STEM image. The Ni (red), O (green) in single distribution and their composition, (b) Left Top: TEM image displaying nanomaterial. Right top: HRTEM image displays the detailed areas of left top

TEM. Left bottom: HRTEM image displaying the twin boundary situated at the red squared region and the corresponding FFT image describes that the nanomaterial exhibits the cubic phase of NiO. Right bottom: HRTEM micrograph indicating a complete structure of the blue squared region and can be seen from the [101] direction, as revealed by the FFT image. (c) EELS chemical information spectrum from the red rectangle part of the ADF-STEM image for the NiO/MoS_x hybrid. Single element spectra and their hybrids are shown (d) NiO/MoS_x system. Left top: TEM micrograph indicating the mapping of the NiO/MoS_x nanohybrid. Middle and Right top: HRTEM image displaying morphology of the NiO nanoplate. Left bottom: HRTEM micrograph of the red squared area and the corresponding FFT image. Right bottom: complete information about interface of the blue squared area and the corresponding FFT image.¹³

Fig.5.5 (a) shows the LSV curves of different catalysts such as GCE, MoS_x, NiO, MoS_x@NiO, and 20% Pt/C at a scan rate of 5 mV/s in 1M KOH bubbled with N₂ gas. The GCE exhibits poor HER activity at (~570 mV vs RHE), in comparison to other materials. The pristine MoS_x shows an HER performance at (~508 mV vs RHE), due to its agglomeration during HER experiment. The HER activity of the NiO is also poor and found at relatively large potential (~535 mV vs RHE). The MoS_x@NiO hybrid catalyst shows HER performance at low overpotential and it gives 10 mA/cm² current density with consumption of 406 mV. This superior performance of the hybrid material is attributed to the synergy between the MoS_x nanosheets and the NiO which enhanced the density of the active sites and excellent charge transport is provided by the NiO nanostructures. The composite system carries an overpotential equal or better than the already developed catalysts CoP/CC (500 mV)¹⁴, N, P-G (700 mV)¹⁵, MoS_x (540 mV)¹⁶, Co-S/FTO (480 mV)¹⁷, and Co-NR CNTs (450 mV).¹⁸ The Pt/C material has overpotential of 110 mV, relatively lower than our composite system, but for a non-noble catalyst the performance is highly encouraging, and it gives a way to design a new class of non-precious materials for water splitting. Our composite has proved itself much better than the pristine MoS_x and NiO.

The HER rate is examined through the linear region of LSV curves using the Tafel equation [Eq. (1)]:

$$\eta = b \log(j) + a \quad (1)$$

Here a signifies a constant connection to exchange current density (j) and b indicates the Tafel value. In basic media, the HER mechanism proceeds through the occurrence of hydrogen adsorbed intermediates (H_{ads}). The electron transfer is involved through the formation of H_{ads} and the discharge of water by Volmer reaction [Eq. (2)]:

The second step in the HER is either via a transfer of another electron which is called Heyrovsky reaction [Eq. (3)]:

or by the Tafel step [Eq. (4)]:

It is a general concept that a Tafel values 120, 40, or 30 mVdec⁻¹ are related to Volmer, Heyrovsky, or Tafel steps.^{19,20,21} A Tafel value 43 mVdec⁻¹ indicates the Heyrovsky step is a rate-determining step in 1M KOH for the MoS_x@NiO hybrid material **Fig.5.5 (b)**. Both NiO and MoS_x also obey Heyrovsky step and the kinetics is governed by electrochemical desorption. A Tafel value of GCE of 105 mVdec⁻¹ and the kinetics is restricted by the Volmer reaction and it indicates the sluggish HER process. The Tafel value for the Pt/C is 30 mVdec⁻¹ which shows that the electrochemical reaction is followed by the Tafel reaction. The Tafel value of our composite system is small compared to the recently reported Ni-consisting catalysts and other catalysts in basic conditions.^{19, 22, 14, 23- 25} Based on the Tafel slope value, in this study, we have the best catalysts so for a basic solution among the reported catalysts and it is important from practical applications. The low Tafel value indicates the efficient HER rate.

Fig. 5.5. (a) LSV curves in N₂ purged 1M KOH at 25°C. **(b)** Estimated Tafel values of various catalytic materials.¹³

Interestingly, in the literature, most of the MoS_x catalysts are developed on conducting materials and they actively involve with a catalytic performance of produced materials. In this way, actual efficiency of the material is under questions. Herein, we used powders loaded on GCE and it avoids the issue of Ni foam and increases the reliability of the results.

To prove the superior HER activity in this study, we carried out an additional study related to the electrochemical surface area from CV experiment **Fig.5.6 (a-f)**. From the linear fitting of the average of the current density against the scan rate, the slope corresponded to the electrochemically active surface area. We found nearly the same value of the electrochemical surface area for NiO, MoS_x and MoS_x@NiO, i.e. $(1.46 \pm 0.02) \times 10^{-4}$ F/cm² for pure MoS_x, $(1.45 \times 10^{-4} \pm 0.03) \times 10^{-4}$ F/cm² for NiO, and $(1.47 \times 10^{-4} \pm 0.03) \times 10^{-4}$ F/cm² for MoS_x@NiO. These results indicate that there is an improvement in the surface area of the hybrid materials and the enhanced HER activity is coming from the synergy between MoS_x and NiO in the composite system.

Fig. 5.6 (a-f). CV curves (a, c, e) against Ag/AgCl as a reference electrode in 1M KOH purged with N_2 gas, and linear fit (b, d, f) for bare NiO (a, b), bare MoS_x (c, d) and $MoS_x@NiO$ (e, f).¹³

Fig.5.7 (a) LSV curves before and after 13 hrs stability experiment in the base. **(b)** Chronopotentiometry stability in the base for 13 hrs at the current density of 10 mA/cm².¹³

Fig.5.7 (a) indicates the LSV curves for the composite system before and after the stability experiment. The hybrid system is very stable and operates without any loss. The stability experiment on the hybrid was performed through chronopotentiometry for 13 hrs. We observed that a slight change in the potential from 490 to 510 mV is enough to retain the current density of 10 mA/cm² and there was no further drop of the potential and it remains nearly constant for the rest of the 11 hours as shown in **Fig.5.7 (b)**.

5.3. An efficient bifunctional electrocatalyst based on nickel iron layered double hydroxide functionalized Co_3O_4 core-shell structure in alkaline media (Paper III)

In this paper, we developed a bifunctional catalyst. Cobalt oxide nanowires were grown on conducting substrate by wet chemical method.²⁶ Then electrodeposition was carried out for the deposition of NiFeLDH onto cobalt oxide. The NiFeLDH decorated cobalt oxide was studied for the chemical composition and found elements are Ni, Fe, Co, and O, it indicates the successful formation of hybrid material as shown in **Fig.5.8**. The distribution of Ni and Fe was homogenous on cobalt oxide nanowires and revealing excellent compatibility of two nanostructured materials.

Fig. 5.8. (a) EDS elemental distribution NiFeLDH decorated on Co_3O_4 nanowires, **(b)** EDS spectra of NiFeLDH decorated on Co_3O_4 nanowires.²⁶

Fig.5.9 shows the XRD reflections of pristine cobalt oxide and core-shell structure obtained from the powder XRD technique. The pure cobalt oxide carries a cubic phase and shows a good crystalline property and fully supported by JCPDS card no. 96-900-5890. After the deposition of the NiFeLDH onto the cobalt oxide nanowires, the intensity of some of the reflection peaks

is suppressed and new reflection peaks for the NiFeLDH have appeared. The reflection peaks of the NiFeLDH are well-matched with reference JCPDS card no. 40-0125. The XRD analysis shows that the pristine cobalt oxide and core-shell system have a similar cubic phase of cobalt oxide and no other impurity was detected.

Fig. 5.9. XRD diffraction patterns (a) bare Co_3O_4 , (b) NiFeLDH decorated Co_3O_4 NWs.²⁶

Fig. 5.10 (a) shows the LSV curves for OER of different catalysts in 1M KOH solution and they are shown without the iR compensation. The base FTO showed negligible OER activity and the pristine NiFeLDH has shown poor OER activity when compared to the bare RuO_2 . However, pure cobalt oxide has shown superior OER performance at low onset potential. The trend of decrease in the onset potential remains prominent when the NiFeLDH were deposited on cobalt oxide nanowires. The synergy is due to Ni, Fe, and Co which is responsible for the superior OER activity for the core-shell nanostructures, as they are catalytically active.²⁷ Further to describe the synergy, the Ni and Fe into the core-shell structure enhanced the quantity of catalytic sites and conduction of the composite material.²⁷ A current density of 40 mA/cm^2 is observed at a potential of 1.49 V vs RHE which is superior to many of the reported perovskite catalysts in the recent time.^{28-32, 33-35} The core-shell nanostructured catalyst has also better OER activity when compared to the cobalt oxide-based catalysts.³⁶⁻³⁸ In OER curves a prominent

redox peak is observed at 1.41 V vs RHE for the core-shell system, which is assigned to the oxidation of Ni, however for pristine NiFeLDH has negligible peroxidation peaks because of a very thin film on FTO substrate as shown in **Fig.5.10 (a)**.

The OER kinetics was investigated through the Tafel study. The Tafel slope was estimated from the linear part of LSV curves. The core-shell system has a Tafel value of 120 mVdec⁻¹ as shown in **Fig.5.10 (b)**, and it is smaller than many of the reported OER catalysts.^{39, 40} The RuO₂ has a Tafel value 101 mVdec⁻¹, the bare Co₃O₄ exhibited a value of 136 mVdec⁻¹ and the NiFeLDH carries a Tafel value of 141 mVdec⁻¹. The high Tafel values are assigned to the self-resistance of the material and the FTO substrate.^{39, 40} The low Tafel value of core-shell confirms the favorable OER activity, it can be connected to the excellent compatibility of the NiFeLDH and cobalt oxide materials.

Fig. 5.10. (a) LSV curves of various materials, bare FTO, RuO₂, pristine NiFeLDH, pristine Co₃O₄, NiFeLDH decorated Co₃O₄ nanowires at a scan rate of 5 mV/s in 1M KOH, (b) the corresponding Tafel values from LSV curves for various materials, (c) LSV curves of different materials, bare FTO, pristine NiFeLDH, pristine Co₃O₄, NiFeLDH decorated Co₃O₄ nanowires, 20% Pt/C at a scan rate of 5 mV/s in 1M KOH (d) the corresponding Tafel values from LSV curves for various materials.²⁶

The HER activity of NiFeLDH decorated cobalt oxide nanowires were also evaluated in 1M KOH by LSV curves at 5 mV/s. The LSV curves of various materials were recorded such as bare FTO, pristine cobalt oxide and NiFeLDH, core-shell system, and 20% Pt/C as shown in **Fig.5.10 (c)**. The HER curves are presented without iR drop. Pt/C has shown superior HER activity as shown in **Fig.5.10 (c)**. However, as a non-precious material composite system, it has also shown a significant HER performance and measures 10 mA/cm² current density at -0.303 V vs RHE which is nearly the same or better to other recently developed HER catalysts. The HER kinetics was evaluated through the Tafel values and Tafel values were calculated from the linear part of LSV curves as depicted in **Fig.5.10 (d)**. The Tafel value of the core-shell structure was 79 mVdec⁻¹ and it obeys the Volmer–Heyrovsky step and restricted by the Heyrovsky reaction step. The observed Tafel slope 79 mVdec⁻¹ is equal or better to many of the reported cobalt-based materials.^{41, 42}

The low Tafel slope reveals the excellent HER activity of the hybrid material and it is believed that the range of Tafel slope is between 60-120 mVdec⁻¹ indicating that the HER occurs on the surface of the catalyst through Volmer–Heyrovsky mechanism.⁴²

5.4. Advanced Co₃O₄-CuO nano-composite based electrocatalyst for efficient hydrogen evolution reaction in alkaline media

(Paper IV)

In this work, we used a facile approach to prepare Co₃O₄-CuO nanocomposite via low-temperature aqueous chemical growth method by introducing a small impurity of copper chloride into cobalt oxide precursor.⁴³ We found a significant increase in the HER activity in a basic environment. Elemental mapping was carried out and Co, O, and Cu were homogenously found in the composite Co₃O₄-CuO. The involvement of Sn is seen from the FTO substrate as shown in **Fig.5.11 (a)**. The relative quantity of each Co, O, and Cu is given into the EDS image **Fig.5.11 (b)**.

Fig. 5.11 (a) EDS elemental distribution a Co₃O₄-CuO hybrid, **(b)** EDS spectra Of Co₃O₄-CuO hybrid.⁴³

Powder XRD measurements were used to explore the phase and purity of various nanostructured materials as shown in **Fig.5.12 (a-c)**. They have very intense reflection peaks

which suggest the good crystalline quality of each material. Besides the grown materials, the FTO reflection peaks are prominent as shown in **Fig.5.12 (a-c)**. The pristine CuO crystalline in a monoclinic phase and the crystalline properties are according to reference card no.96-900-8962. The cobalt oxide has a cubic phase and all the reflections are fully supported by reference card no.96-900-5890. The composite $\text{Co}_3\text{O}_4\text{-CuO}$ carries the diffraction patterns of Co_3O_4 and CuO and they agree with reference cards of bare Co_3O_4 and CuO.

Fig. 5.12. XRD diffraction patterns for different catalytic materials **(a)** bare CuO, **(b)** bare Co_3O_4 , **(c)** $\text{Co}_3\text{O}_4\text{-CuO}$ hybrid.⁴³

The XPS analysis was carried for the $\text{Co}_3\text{O}_4\text{-CuO}$ composite sample as shown in **Fig.5.13 (a)**. The wide scan survey confirms the composition and indicates the Co, Cu, and O. The $\text{Co}2p$ spectrum is given in **Fig.5.13 (b)** and exhibits the satellite peaks at binding energies of 795.06 eV and 779.68 eV related to $\text{Co}2p_{3/2}$, and $\text{Co}2p_{1/2}$, respectively.⁴³ The difference between two $\text{Co}2p$ peaks is 15eV that confirms the existence of Co^{2+} valence state.⁴¹ For O1s two characteristics peaks at 529.66 eV and 531.01 eV are found, which are related to surface oxygen vacancies⁴⁴⁻⁴⁵ as shown in **Fig.5.13 (c)**. **Fig.5.13 (d)** gives the valence states of Cu and $\text{Cu}2p$

spectrum which contains shake-up satellite peaks and they are related to CuO.⁴⁶⁻⁴⁹ The presence of binding energies for Cu2p_{3/2} and the Cu2p_{1/2} at 933.66 eV and 953.65 eV, respectively, revealed the presence of CuO.^{47-49, 50-51} The XPS and XRD finding agree to each other and confirm the existence of the hybrid system. XPS was also carried for the bare cobalt oxide and CuO which are not shown here, it indicates the existence of Co, Cu, and O as main elements. XPS reveals the successful addition of Cu into cobalt oxide nanowires and it has tuned the electronic properties, therefore we observe an enhanced activity for the composite system.

Fig. 5.13. XPS spectra (a) survey spectrum Co₃O₄-CuO, (b) Co 2p of Co₃O₄-CuO, (c) O 1s of Co₃O₄-CuO (d) Cu 2p of Co₃O₄-CuO.⁴³

The HER monitored on the hybrid materials Co₃O₄-CuO in basic solution. The different catalysts were used to modify the surface of the GCE and the HER performance of Co₃O₄-CuO was related to the bare cobalt oxide and CuO and precious 20% Pt/C catalyst. LSV measurements were performed for all catalysts in **Fig.5.14 (a)**. The pristine CuO has shown negligible HER activity because of high onset potential and the cobalt oxide has demonstrated weak activity. On the other hand, the composite Co₃O₄-CuO has described better HER performance with low onset potential as shown in **Fig.5.14 (a)**. The composite Co₃O₄-CuO

requires an overpotential of 288 mV vs RHE to produce a current density of 10 mA/cm² which is relatively close to that of recently published work on CoO.⁵²

The HER kinetics using Tafel slope values was correlated to the recent work⁵² and it has a Tafel value 82 mVdec⁻¹. But our composite system has Tafel value 65 mVdec⁻¹ as depicted in **Fig.5.14 (b)**. The rate-determining step is followed by Heyrovsky's step. The pristine cobalt oxide follows the Heyrovsky mechanism and it has a Tafel value of 94 mVdec⁻¹ which is close to recent research work.⁵² The noble catalyst Pt/C has Tafel value 49 mVdec⁻¹ and it obeys Volmer–Heyrovsky kinetics. The Tafel slopes for the GCE is 328 mVdec⁻¹ and the CuO is 243 mVdec⁻¹. These high Tafel values can be connected to the self-resistance.^{53, 54}

Fig. 5.14. (a) LSV curves for various materials GCE, bare CuO, bare Co₃O₄, and Co₃O₄-CuO hybrid, 20% Pt/C at scan rate of 5 mV/s in 1M KOH, **(b)** the corresponding Tafel values from HER LSV curves for various materials.⁴³

The EIS was done to collect information about charge transport and kinetics from 100 KHz to 0.1 Hz in 1M KOH at an onset potential of 300 mV vs RHE and sinusoidal 10 mV. The Nyquist plots along with equivalent circuits are shown as inset **Fig.5.15 (a)** and Bode plots in **Fig.5.15 (b)** and **Fig.5.15 (c)**. The circuit fitted values are given in Table 1. The equivalent circuit has circuit elements such as solution resistance (R_s), charge-transfer resistance (R_{ct}), and the double-layer capacitance (C_{dl}). The measured charge transfer resistance for the composite is (173.2 Ω) is lower and the composite exhibits a large capacitance C_{dl} (1.97 mF) in comparison to bare CuO and Co₃O₄, thus the composite is highly active for HER. The EIS information is strengthened by existing literature.^{40,55,56}

Fig. 5.15. (a) Nyquist plots at applied potential of -0.3 V vs RHE, a frequency from 100 kHz to 0.1Hz, and amplitude of 10 mV in 1M KOH and Bode (b, c) plots The inset in a graph (a) is the equivalent circuit used to fit the data. R_s solution resistance, R_{ct} charge transfer resistance, and C_{dl} the double layer capacitance.⁴³

Table 1. The fitted values for the elements of equivalent circuit.⁴³

Sample	R_s (Ohm)	R_{ct} (Ohm)	CPE (mF)
$\text{Co}_3\text{O}_4\text{-CuO}$	2.82	173.20	1.97
Co_3O_4	2.04	384.50	0.85
CuO	2.25	656.90	0.35

5.5. Chemically reduced CuO-Co₃O₄ composite as a highly efficient electrocatalyst for oxygen evolution reaction in alkaline media

(Paper V)

In this research work, we chemically reduced a CuO-Co₃O₄ composite and found efficient for OER.⁵⁷ The chemical reduction changed the composition of the CuO-Co₃O₄ composite; therefore, we see only OER activity when we compare it with our previous work (Paper IV). The XRD was applied to understand the composition, crystalline structure, and purity of various nanostructured materials such as Co₃O₄, CuO, CuO-Co₃O₄ and chemically reduced CuO-Co₃O₄ as shown in **Fig.5.16**.

The pristine cobalt oxide and CuO exhibit well-resolved reflection peaks and it indicates the high quality of these materials as shown in **Fig.5.16 (a, b)**. The reflection is supported by (reference card no: 96-900-5890) and the monoclinic phase of CuO (reference card no: 01-089-2529). The pristine CuO-Co₃O₄ composite has both phases of cobalt oxide and CuO. The diffraction patterns are supported by reference cards of cobalt oxide and CuO **Fig.5.16 (c)**. However, powder XRD has shown reflection peaks of copper as cubic phase (reference card no: 96-901-3016), cobalt cubic phase (reference card no: 96-901-1626), Co₃O₄ cubic phase (reference card no: 96-900-5890) and Cu₂O cubic phase (reference card no: 96-900-5770) as shown in **Fig. 5.16 (d)**. Some of the diffraction patterns are also found for the CuO even after reduction. The XRD study shows that the CuO-Co₃O₄ composite is successfully reduced to low valence states of copper and cobalt, thus superior OER activity is found for the reduced composite.

Fig. 5.16. XRD diffraction patterns, (a) Co_3O_4 , (b) CuO , (c) pure CuO - Co_3O_4 hybrid and (d) chemically reduced (T) CuO - Co_3O_4 hybrid.⁵⁷

The porosity of nanostructured materials plays a vital role in water splitting, therefore specific surface area and pore size distribution of untreated CuO - Co_3O_4 and chemically reduced CuO - Co_3O_4 composite was carried out by nitrogen gas adsorption. As depicted in **Fig.5.17** type-IV isotherms were found for both materials and indicating the macro porosity for both samples. The calculated specific surface area through a well-known multi-point BET method was $4.322 \text{ m}^2\text{g}^{-1}$ for the bare CuO - Co_3O_4 , which is lower to that of chemically reduced CuO - Co_3O_4 composite ($15.751 \text{ m}^2\text{g}^{-1}$). Both materials such as CuO - Co_3O_4 and the chemically reduced CuO - Co_3O_4 possess a $2.474 \times 10^{-2} \text{ cc g}^{-1}$ and $8.298 \times 10^{-2} \text{ cc g}^{-1}$ pore volume (**inset in Fig.5.17 a**). Based on the specific surface area it can be said that chemically reduced CuO - Co_3O_4 is more favorable for the OER activity.^{58, 59}

Fig. 5.17. BET analysis, (a) bare $\text{CuO-Co}_3\text{O}_4$ hybrid, (b) chemically reduced $\text{CuO-Co}_3\text{O}_4$ hybrid (Inset is pore size distribution).⁵⁷

The LSV was carried out on Co_3O_4 , CuO , $\text{CuO-Co}_3\text{O}_4$ and chemically reduced $\text{CuO-Co}_3\text{O}_4$ in 1M KOH as depicted in **Fig.5.18 (a)**. LSV was used on RuO_2 and bare glassy carbon working electrode as standard samples. All the potentials were converted to RHE and bare GCE and pristine CuO have shown a negligible OER activity. The OER performance for the Co_3O_4 , pristine $\text{CuO-Co}_3\text{O}_4$ and chemically reduced $\text{CuO-Co}_3\text{O}_4$ composite was found at an onset potential of 251.4 mV, 212.4 mV, and 144.5 mV vs RHE by achieving a current density of 40 mA/cm^2 , respectively.⁵⁷ The pre-oxidation peaks are assigned to copper (I) to copper (II) and cobalt (II) to (III) as shown in **Fig.5.18 (a)** and they have been discussed elsewhere. The chemically reduced $\text{CuO-Co}_3\text{O}_4$ has shown a low onset potential and high current density. The chemically reduced $\text{CuO-Co}_3\text{O}_4$ composite exhibits a small Tafel value of 74 mV dec^{-1} , which is relatively smaller than the value for the pristine $\text{CuO-Co}_3\text{O}_4$ (121 mV dec^{-1}), as shown in **Fig.5.18 (b)** suggesting a swift OER on chemically reduced $\text{CuO-Co}_3\text{O}_4$ composite.

Fig. 5.18. (a) LSV curves at a scan rate of 1 mV/s in 1M KOH, (b) Tafel plots from LSV curves, (c) chronoamperometric stability test chemically reduced $\text{CuO-Co}_3\text{O}_4$ hybrid for 40 hours at 1.39V (versus RHE) in 1M KOH, (d) durability response of chemically reduced $\text{CuO-Co}_3\text{O}_4$ hybrid before and after chronoamperometric stability test.⁵⁷

The durability of the chemically reduced sample was monitored by chronoamperometry for 40 hrs at 1.39 V vs RHE **Fig.5.18 (c)**. Our catalysts tend to work efficiently for more than 40 hours without loss of any activity. The stability experiments were performed before and after the durability experiments and the catalyst maintains its stability and can be used for practical applications as shown in **Fig.5.18 (d)**.

5.6. Electronic and structural disorder in Cu-MoS₂ composite nanostructures for efficient hydrogen evolution reaction in acidic and alkaline media

(Paper VI)

In this research work, we followed a hydrothermal method for the synthesis of pure MoS₂ and Cu induced MoS₂ nanostructures.⁶⁰ An addition of copper as an impurity into MoS₂ has significantly improved its catalytic activity.

Fig.5.19 (A) represents a high-resolution transmission electron microscopy micrograph of various materials including pristine MoS₂ and Cu-doped MoS₂ samples. Pure MoS₂ exhibits excellent crystalline phase and the crystal lattices are indexed to the MoS₂ within the 3R or 2H phases as shown in **Fig.5.19 (a)**. The material induced with 30% of Cu is found to have poor crystalline nature consisting of MoS₂ nanosheets and containing lattice fringes of 6.1 Å spacing and is well matched to the (002) planes. The 2D nanosheets of MoS₂ can be correlated to the (002) fringes of folded edge of vertically structured nanosheets and it can be measured between 1 and 6. The lateral dimension of these fringes is slightly below 5 nm and it indicates a reduced domain size which could be assigned to the copper presence in the sample. However, some of the reflections are observed from the FFT at 2.7 Å, related to the (100) lattice fringes. The small size of the crystal domains can be a cause for the widening of these spots, and it may not allow any further understanding related to Cu integration inside the crystal structure of Molybdenite lattice.

The sample 56% of Cu induced has similar features to that of 30% and 45% Cu samples as shown in **Fig.5.19 (d)**. The EDS analysis shows the presence of Mo, S, and Cu, and they were measured from the FFT of HRTEM images indicating the ammonium thiomolybdate nanoparticles along with MoS₂ nanosheets.

The presence of Cu in the MoS₂ samples was studied by STEM-EDS mapping and pure MoS₂ carries no copper content as expected, however, in the copper-induced MoS₂, copper is uniformly distributed along with Mo and S and showing the presence of substitutional doping into the MoS₂ as shown in **Fig.5.19 (B)**.

Fig. 5.19. (A) HRTEM and FFT images describing the crystal size distribution before and after the doping of Cu in MoS₂. (a) pristine MoS₂, (b) 30% CuMoS₂, (c) 46% Cu MoS₂, (d) 56% CuMoS₂.⁶⁰

Fig.5.19. (B) The elemental mapping for various Cu doped MoS₂ samples. The EDS cumulative spectrum and spatial distribution of the different elements are reported.⁶⁰

We modified the surface of the glassy carbon electrode using pristine and Cu-induced MoS₂ nanostructures and evaluated the HER performance in alkaline and acidic media. We used a three-electrode electrochemical cell system. **Fig.5.20 (a, c)** shows the LSV curves measured at a scan rate of 5 mV/s. The copper induced MoS₂ has shown better HER activity compared to the pure MoS₂. We observed a current density of 10mA/cm² at 0.26V and 0.31V overpotentials in acidic and alkaline conditions for the samples with 30% and 46% Cu-doped MoS₂

electrocatalysts, respectively. The superior performance of copper doped MoS₂ nanostructures can be attributed from addition of copper into the MoS₂ and possible activation of a basal plane which is reported in theoretical results.⁶¹ It has been shown in recent studies that doping is a promising approach to uplift the performance of MoS₂ material.⁵⁸ Different materials have shown different values of the onset potential, overpotential, and current densities. The HER kinetics is well understood by extracting the Tafel values from the LSV curves. The Tafel value is governed by the concentration of active sites, charge transport, and adsorption free energy of hydrogen. The estimated Tafel slope values for the different catalysts are enclosed in **Fig.5.20 (b, d)**.

The Tafel slope of Pt was found to be 31 mV/decade which is well matched to the published results.^{62, 63} The Tafel slope for the presented nonprecious catalysts was estimated to be 86, 56, 75, and 77 mV/decade for the undoped and copper doped samples, respectively. The measured Tafel slopes are in good agreement with the undoped MoS₂.⁶⁴ However, copper doping has a significant contribution towards improved HER performance of the MoS₂. For the noble metal Pt catalyst, the HER kinetics is governed by the Volmer-Tafel reaction and the rate of reaction is determined by the recombination step in acidic conditions. For the sample 30% Cu, the rate of reaction is limited by desorption of H₂, and Volmer-Tafel is the mechanism followed by the samples having 46% and 56% and the Tafel values are in good agreement with published results.^{65, 66} In alkaline conditions, the Tafel slopes are 49,130,42 and 73 mV/decade for the pure MoS₂ and Cu induced MoS₂ nanostructures, respectively, as shown in **Fig.5.20 (d)**. In alkaline media, for the Pt, the rate is limited by the Volmer reaction and its Tafel slope is according to the published works.^{67,68-70} The produced nonprecious catalysts follow the Heyrovsky process (pure MoS₂, 46% Cu, and 56% Cu) or the Volmer–Tafel mechanism (30% Cu). The measured Tafel slope values are in good agreement with earlier reported results.^{66, 67} Interestingly, the Tafel slope of the 46% Cu induced MoS₂ is the lowest for Mo based materials.⁷¹⁻⁷⁴ These experimental findings are consistent with the theoretical study carried on copper doped MoS₂ in which it is suggested that copper is not only substitutionally added, but it has activated the basal plane.⁶¹

Fig. 5.20. LSV curves of different materials at a scan rate of 5 mV/s in (a) N₂ saturated 0.5M H₂SO₄ and (b) the Tafel values from LSV curves various electrocatalyst in acid. (c) LSV curves of various electrocatalysts at the scan rate of 5 mV/s in N₂ saturated 1M KOH, (d) Tafel values from LSV curves for various electrocatalyst in alkaline media.⁶⁰

5.7. References

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CHAPTER 6

Conclusion and Future work

6.1. Conclusion

In this research thesis, based on the obtained results the following conclusions are drawn:

- The nanostructured metal oxides and their composite are synthesized by low-temperature aqueous chemical growth and hydrothermal methods.
- These nanostructured materials are studied for collecting the information about size, shape, purity, and chemical constituents via XRD, Raman, SEM, BET, XPS, HRTEM.
- These nanostructured materials proved as an excellent, earth-abundant, and nonprecious materials for HER/OER either in an acidic or alkaline environment.
- $\text{MoS}_2\text{-TiO}_2$ composite found to be active for HER in basic and acidic conditions and experienced low overpotential (350mV in acidic and 700mV in alkaline conditions), and the corresponding Tafel values in acidic and alkaline conditions are 48 and 60 mV/dec, respectively.
- In the $\text{MoS}_x\text{@NiO}$ composite, HER was noticed with low overpotential 226 mV for 10 mA/cm^2 current density. The Tafel slope value 43 mV/decade, is the lowest MoS_2 -based materials. The composite was found durable for 13 hours.
- The NiFeLDH functionalized Co_3O_4 composite, in the case of HER, produces a current density of 10 mA/cm^2 at -0.303 V versus RHE. While in OER, a current density of 40 mA/cm^2 is measured at a voltage 1.49 V vs RHE.
- The $\text{Co}_3\text{O}_4\text{-CuO}$ nanocomposite has a Tafel slope of 65 mVdec^{-1} which is the lowest for cobalt-based materials. The composite gives out a 10 mA/cm^2 current density at 0.288 V vs (RHE).
- The chemically reduced $\text{Co}_3\text{O}_4\text{-CuO}$ nanocomposite for the OER shows the smallest overpotential 144.5 mV versus RHE to achieve a 40 mA/cm^2 current density. The reduced material is durable for 40 hours.
- In acidic medium, Cu- MoS_2 hybrid measures 10 mA/cm^2 current density at 0.26V versus RHE. In alkaline medium, Cu- MoS_2 composite achieves a 10 mA/cm^2 current density at 0.31V versus RHE.

6.2. Future work

Once upon a time, Richard Feynman demonstrated a lecture and delivered deep words “There is plenty of room at the bottom”. I do agree and believe that following the aspects in the design of efficient catalysts require more attention and they are summarized as below:

- The stability and durability of these non-precious catalysts require more investigations at higher current densities for longer operation durations.
- The Faradic efficiency in terms of O_2 and H_2 production must be monitored.
- The optimization of catalyst ink should be addressed systematically.
- The effect of crystal quality, defect concentrations, and shape of nanostructured materials provide a space that should be investigated soon.
- The material characterization before and after the stability must be performed by XPS and SEM to evaluate the chemical and morphological changes.
- Also, water splitting batteries can be built on these catalysts, and further they can be capitalized for fuel cell technology.

Papers

The papers associated with this thesis have been removed for copyright reasons. For more details about these see:

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