# SYNTHESIZING AND CHARACTERIZING COBALT-MOLEBDYNUM ELECTROCATALYSTS SUPPORTED BY CARBONACEOUS NANOMATERIALS

# SYNTHESIZING AND CHARACTERIZING COBALT-MOLEBDYNUM ELECTROCATALYSTS SUPPORTED BY CARBONACEOUS NANOMATERIALS

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# TITLE: Synthesizing and Characterizing Co-Mo Electrocatalysts Supported by Carbonaceous Nanomaterials

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### Abstract

This thesis explores the synthesis, characterization, and electrochemical behavior of nanocomposites composed of cobalt (Co) and molybdenum (Mo) deposited onto graphene oxide (GO), COOH-functionalized multi-walled carbon nanotubes (CNT-COOH), and blends of these two graphitic nanomaterials. The study aims to investigate the structural, morphological, and electrocatalytic properties of these nanocomposites synthesized via a hydrothermal method. Using a combination of analytical techniques including Raman Spectroscopy, Scanning Electron Microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX), X-ray Photoelectron Spectroscopy (XPS), Cyclic Voltammetry (CV), Chronoamperometry, and UV-vis Spectroscopy, the nanocomposite structures were comprehensively characterized.

SEM imaging demonstrated differential deposition of CoMo particles, demonstrating higher affinity and deposition on CNT-COOH compared to GO. EDX and XPS findings confirmed successful deposition of Co and Mo sulfides and oxides on both supports. According to XPS data, cobalt sulfides, molybdenum dioxide, and molybdenum disulfide were the dominant species synthesized in CoMo-CNT-COOH and CoMo-GO, whereas the prevalent species in CoMo-CNT-COOH-GO were cobalt and molybdenum sulfides. Electrochemical analyses, particularly CV tests, unveiled unique electro-oxidative activity of CoMo-CNT-COOH for Methyl Orange (MO) analyte at -0.4 V. CoMo-CNT-COOH exhibited approximately 68% optimum electrooxidation of MO after 5 hours for 100 mL solution initially made of 30 ppm MO and 0.5 molar sulfuric acid, indicating potential for environmental remediation applications.

Keywords: Cobalt, Molybdenum, electrocatalyst, electrochemical oxidation, methylene orange

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### Contents

Chapter 1. Introduction and Literature Review 1
1.1. General background
1.2. Desulfurization techniques
2.1.1. Adsorptive desulfurization
2.1.2. Activated Carbon7
2.1.3. Oxidative desulfurization (ODS)10
2.1.4. Hydrodesulfurization (HDS)11
2.1.5. Biodesulfurization (BDS)15
2.1.6. Electrochemical desulfurization
1.3. Comparing the desulfurization methods
1.4. Objective of the current work
1.5. Thesis outline
Chapter 2. Co-Mo catalysts on carbonaceous nanomaterials
2.1. Materials
2.2. Devices used for preparations
2.3. Catalyst Preparation
2.3.1. CNT-supported Catalyst
2.3.2. GO-supported Catalyst
2.3.3. GO-CNT-supported Catalyst

2.4. Ink preparation
2.5. Electrode preparation
2.6. Catalyst Characterization
2.6.1. Raman Spectroscopy
2.6.2. SEM and EDX
2.6.3. XPS
2.7. Electrochemical Measurements
2.8. Raman Spectroscopy
2.9. Scanning Electron Microscopy (SEM)
2.10. EDX
2.11. XPS
2.12. Cyclic Voltammetry
2.12.1. Cyclic Voltammetry in supporting electrolyte
2.12.2. Cyclic Voltammetry in analyte
2.13. Chronoamperometry
2.14. UV-vis Spectroscopy
Chapter 3. Significant Contribution and Recommendations
3.1. Key findings and contributions
3.2 Recommendations and Future Works
References

### List of Figures

Figure 1 Common sulfur species in heavy oil [4]2
Figure 2 comparing reactivity of different sulfur-containing molecules in HDS process
[4]12
Figure 3 HDS mechanisms including DDS and HYD paths on Alumina-supported CoMo
catalyst [9]13
Figure 4 photos of autoclave used for synthesis of nanocomposites and the product
containing the nanoparticles of CoMo on the carbonaceous support and unreacted species (i.e.
after synthesis and before washing)
Figure 5 The prepared ink and the FTO glass slides before casting
Figure 6 A set of drop-casted electrodes before and after evaporating the solvent and
getting dried on hot plate at ~70 °C for ~7 hours
Figure 7 The picture of the electrochemical reactor used in this work including three-
electrode configuration including Ag/AgCl electrode as the reference electrode, platinum coiled

Figure 10 SEM images and particle size distribution for the synthesized nanocomposites
CoMo-GO, CoMo-CNT-COOH, CoMo-GO-CNT-COOH 40
Figure 11 Energy Dispersive X-ray Scanning Spectroscopy (EDX) on mapping mode for
CoMo-GO confirming the presence of Co, Mo, S, O, and C in CoMo-GO and the elements
distribution across the area shown in the image
Figure 12 Energy Dispersive X-ray Scanning Spectroscopy (EDX) on mapping mode for
CoMo-CNT-COOH confirming the presence of Co, Mo, S, O, and C in CoMo-GO-CNT-COOH
and the elements distribution across the area shown in the image
Figure 13 Energy Dispersive X-ray Scanning Spectroscopy (EDX) on mapping mode for
CoMo-GO-CNT-COOH confirming the presence of Co, Mo, S, O, and C in CoMo-CNT-COOH
and the elements distribution across the area shown in the image
Figure 14 XPS Scan survey on CNT-COOH45
Figure 15 carbon peaks in CNT-COOH XPS survey
Figure 16 XPS scan survey for graphene oxide
Figure 17 carbon peaks in GO XPS survey
Figure 18 XPS scan survey for CoMo-GO 48
Figure 19 Survey on S2p, Co2p, C1s, and Mo3p in CoMo-GO 49
Figure 20 XPS scan survey for CoMo-CNT-COOH 50
Figure 21 C1s, S2p, Co2p3, and Mo3p3 peaks in CoMo-CNT-COOH spectrum 51
Figure 22 XPS survey for CoMo-GO-CNT-COOH
Figure 23 C1s, S2p, Co2p3, and Mo3p3 peaks in CoMo-GO-CNT-COOH spectrum 53
Figure 24 cyclic voltammetry plots with 0.2 V/s scan rate in three-electrode

configuration, including platinum coil as the counter electrode, Ag/AgCl reference electrode, and

different working electrodes (GO, CNT-COOH, CoMo-GO, CoMo-CNT-COOH, CoMo-GO-

CNT-COOH, CoMo-GO&fCN conducted in a 0.5 molar sulfuric acid solution as electrolyte ... 56

Figure 25 Schematic picture of GO, and sulfonated GO structures, adapted from [90]... 57

### List of Tables

Table 1 Sulfur content in crude oil resources across the world [4]
Table 2 Allowable sulfur content in diesel and gasoline in a few countries across the
world [9]5
Table 3 Reviewing a few Mo-based catalyst applicable in HDS
Table 4 desulfurization techniques comparison [9], [12]–[15], [47], [55]–[57]19
Table 5 The most important properties for COOH-functionalized graphitized multi-
walled carbon nanotubes reported by the manufacturer (cheaptubes.com)
Table 6 The most important properties for GO dispersion used in this research, reported
by the manufacturer (Graphenea)
Table 7 List of laboratory devices used in catalyst preparation, ink and electrode
preparation
Table 8 The nanocomposites synthesized and investigated in this study
Table 9 compositional information gained by EDX characterization test for all three
nanocomposites, including CoMo-GO, CoMo-CNT-COOH, CoMo-GO-CNT-COOH

# **Chapter 1. Introduction and Literature**

# Review

#### 1.1. General background

Despite all the efforts to replace fossil fuels with green energy resources, crude oil and natural gas are still the dominant energy resources worldwide. Crude oil is refined into various fossil fuel products, such as gasoline, and diesel which are increasingly demanded by transport and industry sectors [1]. The sulfur concentration and the type of sulfur-containing compounds in crude oil vary significantly from one region to another. Table 1 reports approximate sulfur contents in crude oil extracted from oil resources in different territories, ranging from 0.4 wt% to 8.4 wt%.

Sulfur compounds, in crude oil and the fuels derived from crude oil, include the simplest components like sulfides, disulfides, and thiols, and the aromatic sulfur family widely known as thiophene components like Thiophene (TH), Benzothiophene (BT), and Dibenzothiophene (DBT), depending on the source of fuel [2], [3]. Figure 1 introduces the eight main sulfur-containing species present in heavy oil sources, for instance.



Figure 1 Common sulfur species in heavy oil [4]

Generally, sulfur-containing components impose detrimental effects on industry, the environment, and health [5]. From an environmental perspective, sulfur components in the fuel are oxidized to sulfur-oxide components (SO<sub>x</sub>) during combustion and released into the atmosphere through exhaust gas. SO<sub>x</sub> can damage the ozone layer or enter the soil and water resources by acidic rain and pollute those resources. From a health perspective, long-term exposure to SO<sub>x</sub> components can threaten human health and cause serious diseases like cancer. From an industrial viewpoint, sulfur can cause corrosion in pipelines and equipment, and inactivate catalytic active sites on catalytic processes through poisoning [6]–[8].

Due to the reasons mentioned above, and the fact that petroleum fuel products are still inevitable, the world is pushing towards higher-quality fossil fuel products with controlled sulfur pollutants content. Regulatory bodies introduce strict sulfur content regulations and hefty fines to compel industries to reduce sulfur content in their product or in their wastewater to an allowable low-risk level. For instance, Table 2 illustrates the allowable sulfur concentration in gasoline and diesel in a few countries. Therefore, all the industry, environment, and health sectors are in agreement to implement measures to separate sulfur components from crude oil, downstream or later from the exhaust gas, to avoid releasing sulfur into the atmosphere.

So far, several methods have been introduced as effective sulfur separation processes, including physical methods like adsorption and extraction; chemical methods like oxidation and alkylation, and hydrodesulfurization; biological methods like enzymatic biodesulfurization and electrochemical methods like electrochemical oxidation [9].

3

Oil type	Sources	Sulfur (wt%)
Heavy oil	Mexico, Maya	3.52
Extra-heavy oil	Canada, Athabasca	7.95
Extra-heavy oil	Canada, Alberta	5.10
Heavy oil	Venezuela, Boscan	3.50
Heavy oil	Iran, Soroush	4.80
Heavy oil	Mexico, Veracruz	4.81
Heavy oil	Iran, Gachsaran	2.60
Heavy oil	USA, Oxnard, California	7.47
Extra-heavy oil	Venezuela, Hamaca	1.55
Extra-heavy oil	China, Liaoche	0.42
Heavy oil	Canada, Cold Lake	7.14
Heavy oil	Canada, Lloydminster	4.3
Heavy oil	Iraq, Qayarah	8.4
Heavy oil	China, Bamianhe, Shengli	1.87
Shale oil	China, Huadian	3.14
Waste tire oil	China	1.50

#### Table 1 Sulfur content in crude oil resources across the world [4]

Country	2005	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
US1		30 ppm										
US <sup>2</sup>		15 ppm										
EU <sup>1</sup>				10 ppm								
EU <sup>2</sup>				10 ppm								
Japan <sup>1</sup>			10 ppm									
Japan <sup>2</sup>			10 ppm									
Australia <sup>1</sup>				10 ppm								
Australia <sup>2</sup>				10 ppm								
China <sup>1</sup>								10 ppm				
China <sup>2</sup>									10 ppm			
Korea <sup>1</sup> , Republic of				10 ppm								
Korea <sup>2</sup> , Republic of				10 ppm								
India <sup>1</sup> (selected cities)					50 ppm							
India <sup>1</sup> (rest of the nation)						150 ppm						
India <sup>2</sup> (selected cities)					350 ppm							
India <sup>2</sup> (rest of the nation)						50 ppm						
Brazil <sup>1</sup>									500 ppm			
Brazil <sup>2</sup>									50 ppm			
Singapore <sup>1</sup>								50 ppm				
Singapore <sup>2</sup>								10 ppm				
Thailand <sup>1</sup>							50 ppm					
Thailand <sup>2</sup>							50 ppm					

Table 2 Allowable sulfur content in diesel and gasoline in a few countries across the world [9]

Data extracted from the Ministry of Petroleum and Natural Gas 2014, ASEAN 2016, International Energy Agency 2016. <sup>1</sup>Sulfur content in gasoline.

<sup>2</sup>Sulfur content in diesel.

#### **1.2.** Desulfurization techniques

Desulfurization techniques are crucial for improving fuels quality and minimizing sulfur-based pollutants emissions. These methods can be categorized into physical, chemical, and biological approaches. Physical desulfurization mainly uses methods such as adsorption, where sulfur compounds are trapped on solid substrates, effectively isolating them from the hydrocarbons. In chemical strategies, a reducing or oxidizing agent is used to react with sulfur-containing hydrocarbon. In particular, during hydrodesulfurization (HDS), the fuel is processed at elevated pressures and temperatures using catalysts, transforming sulfuric elements into hydrogen sulfide. Another chemical technique is Oxidative Desulfurization (ODS), which oxidizes sulfur compounds into sulfones using an oxidizing agent (ozone, hydrogen peroxide, peroxy acid) at low pressure and temperature. Biodesulfurization (BDS) uses specific microorganisms to selectively eliminate sulfur while preserving the energy quality of the fuel because the microorganism does

not decompose hydrocarbon backbone. These dominant desulfurization techniques are discussed and briefly reviewed hereafter [1], [5], [7], [9]–[14]. Electrochemical oxidation of sulfurcontaining pollutants has gained a huge attention from science community due to its potential for degrading such pollutants at low pressure and temperature. Through the utilization of electrochemical electrooxidation and the enhancement of kinetics via electrocatalysis, sulfurcontaining contaminants can be effectively converted into less harmful substances, thereby contributing to less environmental contamination, including cleaner air and water [15].

#### 2.1.1. Adsorptive desulfurization

Adsorptive desulfurization (ADS) is a method by which sulfur compounds from fuels are adsorbed on or into a solid adsorbent. Activated carbon, Metal Organic Frameworks (MOFs), Silica, Zeolite, Graphene, carbon fibers (CF), and polymeric adsorbents are the most common adsorbents used in desulfurization. Unlike hydrodesulfurization (HDS) method that requires extreme conditions of elevated temperature and pressure, ADS is applicable at ambient temperature and pressure. However, in practice high pressures and temperatures are used in the ADS process to increase adsorption extent and kinetics. Material selections for adsorbents plays a vital role in maximizing the effectiveness of sulfur-containing component separation. Besides, adsorption capacity can be promoted by adjusting pore size, distribution of active adsorption sites, porosity, and surface interaction with the adsorbate molecules. Like all adsorption processes, ADS can occur through physisorption or chemisorption, depending on the strength of interactions between the adsorption sites and the sulfur compounds. Surface modifications such as functionalization can alter such interactions and improve adsorption capacity [10], [12], [16], [17].

#### 2.1.2. Activated Carbon

Activated carbon (AC) is a sustainable adsorbent for sulfur compounds with high surface area and can be derived from various renewable and non-renewable precursors. The adsorption capacity usually improves by bounding oxygen-containing functional groups on AC surface or introducing metal oxide species on AC as the support for active sites [12].

Sikarwar et al. [18] investigated the use of cobalt-modified activated carbon treated with acetic acid as an adsorbent for ADS of dibenzothiophene (DBT). This modification enhanced the activated carbon's adsorption capacity, and the reason could be due to introducing oxygen-containing functional groups and acidic sites to AC. The highest DBT removal was ~92% for 500 ppm initial concentration. The results also showed that after the introduction of cobalt and acid treatment, the surface area of AC rose from 257 m<sup>2</sup>/g to 393.8 m<sup>2</sup>/g that could have positive effect on the adsorption capacity.

Ganiyu et al. [19] doped AC with varying aluminium concentrations (from 0.05 to 10 wt%) and studied how varying aluminium concentration on AC affects the desulfurization capabilities of dibenzothiophene (DBT). The activated carbon doped with aluminium demonstrated superior adsorption capacity compared to pristine activated carbon. Specifically, the adsorbent sample doped with 2.5% Al concentration achieved the highest separation of 95% for a 200 ppm DBT initial concentration (14.19 mg/g as capacity). A significant reason for the improved desulfurization performance was identified as the tetrahedral coordination of aluminium in the AC-Al composite.

Xiong et al. [20] deposited zirconium dioxide into activated carbon using a hydrothermal method. The ZrO<sub>2</sub>/AC was evaluated for its efficiency in removing dibenzothiophene (DBT) from a diesel fuel. The findings revealed that incorporating ZrO<sub>2</sub> increased adsorption capacity by approximately 17% compared to pristine AC.

#### Metal Organic Farmwork (MOF)

MOFs, particularly those with open metal sites and affinity towards sulfur, exhibit high adsorption capacities for sulfur compounds, outperforming many conventional adsorbents like activated carbon or zeolites. MOFs are well-known for high surface areas, tunable pore sizes, and flexible functional groups. However, this interesting family suffer from high cost and low yield of production and many research groups are working on improving MOFs properties [21].

Ghassa et al. [22] investigated the effectiveness of a composite material synthesized by integrating activated carbon (AC) with a chromium-based MOF(MIL-53(Cr)) in adsorptive desulfurization of dibenzothiophene (DBT) in n-octane. Different composites with various AC concentration from 0% to 10% were synthesized and the composite containing 2.5% AC loaded in MIL-53(Cr) exhibited the highest adsorptive desulfurization efficiency of 95.88% for a solution with 1500 ppm  $S^{1}$ .

Zhu et al. [23] synthesized MOF-5, a zinc-based MOF, on AC and evaluated the resulted composite adsorption performance for a liquid fuel containing sulfur-containing model molecules such as thiophene (Th), benzothiophene (BT) or dibenzothiophene (DBT), sulfides, mercaptan in n-heptane. The results revealed that the MOF-5 to AC ratio significantly affects physical properties of the composite like porosity and morphology, and the surface chemistry of composite leading to desulfurization properties. The composite having a MOF-5 to AC ratio of 1:5 demonstrated optimal desulfurization performance, especially for aromatic sulfur species.

<sup>&</sup>lt;sup>1</sup> parts per million weight sulfur

#### Zeolite

Zeolites are another adsorbent candidate for adsorptive desulfurization. This large aluminosilicate family possesses high surface area and strong acid sites, making them more effective than AC and MOFs in ADS. However, there have been many efforts to improve zeolite performance in ADS through ion-exchange, functionalization, or making composite materials comprising zeolites and carbon or MOFs (for instance) that can produce synergistic effects [24], [25].

Hernandez-Maldonado et al. [26] modified a Y-type zeolite with Cu, Ag, Na, H to make a  $\pi$ complexation zeolite. Adsorption through  $\pi$ -complexation mechanism is stronger than Van der
Waals but weaker than covalent bonds, making this mechanism ideal for both adsorption and
regeneration. Some metal ions can create such interactions with electrons in  $\pi$ -orbitals of aromatic
sulfur molecules. Based on the results, Cu-modified Y-type-zeolite showed the best adsorption
capacity by ADS of thiophene in n-octane.

#### Graphene

Graphene is a single layer of carbon atoms arranged in a 2D hexagonal lattice and has drawn significant attention from the scientific community, due to its outstanding electrical, thermal, and mechanical properties, for various application. For ADS purposes, graphene (G), graphene oxide (GO), reduced graphene oxide (rGO), functionalized-graphene (f-G), metal-graphene composites, nanocomposite of graphene and MOF or zeolite can be different types of graphene-based adsorbents that adsorb sulfur compounds [27].

Zhang et al. [28] aimed to improve DBT removal efficiency through applying surface functionalization on GO and reducing the resulting f-GO to reduced f-rGO. The use of dodecyl amine as a functionalizing agent made the GO more water repellent, which helped prevent graphene layers from clustering together during the reduction process. More extensively reduced graphene showed better sulfur (DBT) adsorption, and this is mostly because the  $\pi$ -complexation adsorption mechanism is stronger on more reduced rGO compared to less reduced rGO.

#### 2.1.3. Oxidative desulfurization (ODS)

Oxidative desulfurization involves the oxidation of sulfur compounds (e.g., thiophenes) to their corresponding sulfones or sulfoxides using oxidants. The oxidized compounds are more polar and can be separated using methods like extraction. Common oxidants include hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), ozone (O<sub>3</sub>), and organic peroxides. ODS with advanced techniques such as ultrasound, plasma, and microwave can significantly enhance sulfur removal efficiency. Combining Ultrasound and ODS promotes efficient reactant dispersion, and thus better possibility of collision between reactants improves the reaction rate. Combining Plasma and ODS utilizes ionized species for more efficient oxidation reactions. And finally simultaneous microwave radiation and ODS offers more kinetic energy to reactants and thus accelerates the oxidation reactions. Moreover, catalysis can enhance the oxidation rates. Metal catalysts (e.g., Mo, W), acidic catalysts (e.g., zeolites, ionic liquids), and photocatalysts have been explored for this purpose [5], [11], [14], [29].

Oxidizing agents like hydroxide radicals in chemical oxidative desulfurization originate from ozone or peroxide containing species, but such agents can also be produced in reaction environments by a photocatalyst. Photocatalytic oxidation desulfurization (PODS) employs photocatalysts to initiate radical-driven reactions that break down sulfur-rich pollutants. When these photocatalysts are exposed to sufficient energy, electrons move from the valence band to the conduction band. This movement creates positive holes and surplus electrons that engage in redox reactions. In the presence of oxygen, these electrons produce radicals such as anionic oxygen radical and hydroxyl radical. These radicals then oxidize sulfur compounds into less harmful

substances. The recent surge in PODS research highlights its growing relevance and the need for comprehensive studies in this area [30].

Dong et al. [31] synthesized a bimetallic oxide catalyst made of Cobalt Molybdenum Oxide composite for catalytic oxidation of DBT by oxygen as oxidizing agent. The results showed synergism between cobalt and molybdenum in CoMoO catalyst.

Gu et al. [32] treated MOF-808(Zr) with hot ethanol to create defects on zirconium metal centers, making MOF-808(Zr)-H that is an active catalyst for ODS of DBT. The defected MOF removed 99% of DBT content (from 1000 ppm to below 10 ppm) in just 20 minutes at approximately 50°C. This material significantly outperformed the original MOF-808(Zr).

#### 2.1.4. Hydrodesulfurization (HDS)

Hydrodesulfurization is the most common method having been used to remove sulfur from liquid fuels such as gasoline and diesel with high efficiency. During this process, the fuel is treated in a hydrogen atmosphere at elevated pressures (typically ranged 3 to 6 MPa) and temperatures (mostly in range of 300–400°C) and with the aid of a catalyst that is usually a molybdenum-based and or tungsten-based catalyst (often combined with cobalt (Co) or nickel (Ni) as the promoters) on an alumina support. The appropriate temperature and pressure depend on the required degree of desulfurization and the complexity of the sulfur-containing molecule. The main goal is to transform unwanted sulfur-based compounds like thiols, sulfides, and thiophenes into hydrogen sulfide under the mentioned reaction conditions. Generally, HDS is more effective for the desulphurization of simple molecules rather than complex ones. Figure 2 illustrates the fact that complex sulfur compounds demand higher temperature and pressure in HDS process to produce hydrogen sulfide, making HDS more expensive. Briefly speaking, the process involves changing

a carbon-sulfur (C-S) bond to a carbon-hydrogen (C-H) bond on a catalyst surface through a series of molecule adsorption on active site, C-S bond breakage, C-H bond formation, and product release from the catalyst. However, the HDS kinetics is not simple but complex with multiple reactions happening simultaneously and depends on sulfur-containing molecule chemistry and catalyst physiochemical properties. For example, dibenzothiophene (DBT), a typical sulfur compound in diesel, can undergo HDS through two main pathways: direct desulfurization (DDS) and hydrogenation (HYD). Figure 3 depicts DDS and HYD reactions during hydrodesulfurization of DBT on the conventional HDS catalyst of Cobalt-Molybdenum supported by Alumina. The preferred route depends on the choice of catalyst and how the process is operated. Efforts are being made to find new catalysts and refine the process to enhance the removal of sulfur compounds, especially those that are more resistant to existing methods [4], [9], [33]–[35].



Figure 2 comparing reactivity of different sulfur-containing molecules in HDS process [4]



Figure 3 HDS mechanisms including DDS and HYD paths on Alumina-supported CoMo catalyst [9]

The first three rows of transition metals have the potential to act as the active catalyst in hydrogenation of sulfur species due to their electron conditions in s and d orbitals. Especially noble metals (including Ru, Rh, Pd, Ag, Os, Ir, Pt, Au) can catalyze HDS in mild temperatures. However, noble metals and most of the other transition metals are not as favourable as conventional HDS catalysts including Molybdenum Sulfide (MoS<sub>2</sub>) and Tungsten Sulfide (WS<sub>2</sub>), due to the cost of noble metals and their potential for poisoning by sulfur. Cobalt or nickel usually accompany the main active metal phase as the promoters, for several purposes including assisting in adsorption of reactants or desorption of products, minimizing catalyst poisoning, improving catalyst stability, enhancing catalyst activity, increasing active sites dispersion, to name but a handful. The metallic active sites and promoters are supported by a porous support with special characteristics including high mechanical strength, high surface to volume ratio, high number of acidic sites for metal dispersion, and having a moderate interaction between metal and support ensuring effortless sulfidation of main phase. The common supports for HDS catalysts are alumina, silica, zeolite, carbon, and metal oxides (known as multi-metallic catalyst) [40]. Table 3 reviews a few molybdenum-based catalysts promoted by cobalt or nickel and supported by different porous materials.

		BET	Temperature	_		Initial sulfur				
Catalyst	Synthesis	Surface	remperature	Pressure	Sulfur	concentration	Decetor true	% sulfur	Reference	Year
	method	$m^2/g$	(°C)	(bar)	compound	(mg/L)	Reactor type	Conversion		
	Derry					(8/)				
	Dry									
CoMo/boron-	impregnation-				FCC		continuous			
modified γ-	sulfidation-	292	260	20	<sup>2</sup> gasoline	510	fixed bed	97	[36]	2021
Al <sub>2</sub> O <sub>3</sub>	microwave				9					
	treatment									
MoNi/	Wet									
Alumina -	impregnation	214	300	50	DBT	500	Batch	99	[37]	2021
CNT	1.0									
CoMo/	Wet									
zeolite-active	impregnation	389	300	50	DBT	500	Batch	98	[38]	2020
carbon	1.0									
	Wet						Fixed bed			
NiMo/c-Al <sub>2</sub> O <sub>3</sub>	impregnation-	183	280	40	DBT	7300 <sup>3</sup>	microreactor	100	[39]	2020
	sulfidation						meroreactor			
	vacuum									
CoMo/C	freeze drying-	148	300	30	DBT	7790 <sup>4</sup>	Batch	95	[40]	2022
	sulfidation									
Mo-										
Co/Zeolite		257						91		
Mo-Ni/Zeolite		245						90	-	
Mo-	Dry								-	
Co/Zeolite-	impregnation-	323	300	55	DBT	550	Batch	98	[41]	2020
graphene	sulfidation									
Mo									-	
Ni/Zoolito		210						07		
NI/Zeolite-		312						97		
graphene										

#### Table 3 Reviewing a few Mo-based catalyst applicable in HDS

<sup>&</sup>lt;sup>2</sup> fluid catalytic cracking (FCC) gasoline
<sup>3</sup> 1% wt DBT in n-decane
<sup>4</sup> 1% wt DBT in cyclohexane

#### **2.1.5. Biodesulfurization (BDS)**

Although the conventional desulfurization methods like hydrodesulfurization are effective in reducing sulfur content, none of them are environmentally friendly. Biodesulfurization is the green approach employing microorganism to selectively remove sulfur elements from hydrocarbons, ensuring the fuel's energy content remains unchanged. This process is cost-effective since it does not require consuming energy to provide special reaction conditions like high temperature and pressure. However, the reaction rate in this method is significantly slower than chemical desulfurization methods. Besides, BDS is not as efficient as chemical methods like HDS, and there would be a long way to enhance the BDS efficiency. Integrating BDS with other sulfur removal techniques could offer a possible solution to the low-efficiency and slow-rate issues [42]–[44].

Yi et al. [45] applied ultrasonic radiation to DBT before undergoing the BDS process and the results showed that integrating ultrasonic radiation and BDS substantially improved the BDS efficiency, with higher sulfur removal rate.

#### **2.1.6. Electrochemical desulfurization**

During Electrochemical Desulfurization (ECDS) techniques, oxidation or reduction electrochemical reactions are employed to degrade sulfur-containing species. These methods typically operate at ambient temperature and pressure, offering high selectivity and activity. However, they often require pH adjustment, pose challenges in electrode selection, and demand optimization of electrolyte concentration. Electrocatalysis significantly influences and enhances these electrochemical systems. Various catalysts, such as Ce and Pt, have exhibited electrocatalytic behavior, as documented in literature [46]. The organic sulfur-containing molecules can be eventually reduced to mineral  $H_2S$  molecules through an electrochemical reduction reaction on the cathode surface. However, the produced  $H_2S$  is a toxic molecule (mineral sulfur containing pollutant), and another separation process is necessary to call the whole separation process a reasonable solution. On the other hand, electro-oxidation of such species at the end of the day can produce sulfate  $(SO_4^{-2})$ , sulfone (R-S(=O) (=O)-R') and sulfoxide (R-S(=O) -R') which are less environmentally harmful than H<sub>2</sub>S. In alkaline and acidic electrolyte, the oxidizing agents are oxygen-containing oxidants (like oxygen, anionic oxygen radical, hydroxyl radical) and metal ions, respectively. During this oxidation process, the metal ion is reduced from higher-valance number to lower-valance number by accepting electron from the target molecules. Various singlemetallic, bimetallic or trimetallic electrocatalysts from d-band group (such as Fe, Mn, Mo, Co, Cu, Ni, Au, Pd, Pt, etc.) can catalyze the oxidation of the target molecules with accelerated kinetics [47], [48].

Xiao-dong Tang et al. [49] proposed a combination of electro-oxidation and extraction to desulfurize kerosene. They used graphite for both the anode and cathode electrodes and sodium chloride solution as the supporting electrolyte. In such systems,  $Cl_2$  and  $ClO^-$  that can be produced by oxidizing chloride ions at anode surface could be the possible oxidizing agents to attack sulfur containing molecules and degrade them. This electrochemical sulfur oxidizing process was followed by extracting the sulfur-containing products by N-methyl-2-pyrrolidone (NMP).

Jing-Jing Li et al. [50] proposed using electrochemical oxidation followed by distillation to desulfurize kerosene and gasoline. They also used graphite electrodes and sodium chloride supporting electrolyte as the electrochemical system, but distillation as the secondary process to remove the products from the fluid.

In another study conducted by Xiao-dong Tang et al. [51], a solution comprising manganese (II) sulfate and sodium sulfate was utilized as the supporting electrolyte. Within this electrochemical setup, a copper electrode functioned as the cathode, while a lead electrode served as the anode.

The resulting products from this electro-oxidation desulfurization process were subsequently extracted using NMP. The research introduced MnOOH (manganese oxyhydroxide) as a potential oxidizing agent within this electrochemical system. MnOOH could be generated through the following reaction at the anode surface:

$$Mn^{+3} + H_2O + O_2 \rightarrow MnOOH$$

Then, this oxidizing agent could be reduced to lower valence and oxidize the sulfur-containing organic molecules to sulfoxide, sulfate, or sulfone.

Zeinab Alipoor et al. [46] investigated desulfurization of thiophene through electro-oxidation on platinum anode surface while using sulfuric acid and perchloric acid mixture as the supporting electrolyte. The results showed the designed electrochemical system was able to desulfurize 466 ppm thiophene to sulfate ion with 100% conversion.

Yadollah Tavan et al. [52] studied electro-oxidation of crude oil on copper electrode in different operational conditions. Their findings indicated that the desulfurization conversion rate could be significantly enhanced under conditions of elevated temperature, increased electrolyte concentration, higher potential, and greater stirring speed.

Xiaoqing Du et al. [53] electrodeposited cerium oxide onto a commercial porous anodic alumina, utilizing it as the anode electrode for the desulfurization process of diesel fuel. Their investigation assessed various factors' impact, including time, potential, electrode surface area, the quantity of supporting electrolyte, and the volume of diesel, on the reaction conversion.

The results highlighted that an increased electrode area positively influenced the conversion rate, while voltage and temperature exhibited optimum levels for effectiveness. Furthermore, augmenting the ratio of electrolyte volume to diesel volume had a beneficial effect on the conversion rate. Notably, the process conversion initially increased but eventually reached a plateau with prolonged electro-processing time.

Wenbo Wang et al. [54] introduced a fluidized-bed reactor for electrochemical oxidation of gasoline. The cathode was a copper rod, and the anode was a bed of carbon-supported cerium oxide particles suspended by a flow of electrolyte-gasoline mixture. They studied the effect of electrolyte (cerium nitrate) concentration, gasoline flow rate, catalyst quantity and applied potential. Under optimal conditions, their findings demonstrated an 84% sulfur removal percentage, showcasing the efficiency of the electrochemical process in the fluidized-bed reactor for gasoline desulfurization.

### **1.3.** Comparing the desulfurization methods

To sum up, Table 4 compares ADS, ODS, HDS, and BDS methods as the most common

desulfurization techniques.

Desulfurization technique	Advantages	Disadvantages			
Adsorptive Desulfurization	<ul> <li>✓ Selective removal of specific sulfur species.</li> <li>✓ Operates at mild conditions (T and P)</li> <li>✓ No need for hydrogen</li> </ul>	<ul> <li>Requiring regeneration process (consuming energy and chemicals)</li> <li>Need another separation process to remove the transferred molecules from regeneration fluid.</li> <li>Low efficiency at high sulfur levels (limited adsorption capacity)</li> <li>Adsorption selection is challenging (since the selectivity and capacity of adsorption is case-dependent)</li> </ul>			
Oxidative Desulfurization	<ul> <li>✓ Applicable to wide range of sulfur compounds</li> <li>✓ Operates at mild conditions (T and P)</li> <li>✓ No need for hydrogen</li> </ul>	<ul> <li>Requires external oxidants (additional cost)</li> <li>Corrosion issues due to strong oxidizing agent</li> </ul>			
Biodesulfurization	<ul> <li>✓ Environmentally friendly</li> <li>✓ No degradation in hydrocarbon (maintaining the energy value)</li> </ul>	<ul> <li>Slower kinetics (unfeasible scale-up)</li> <li>Sensitive to operational conditions (T, pH)</li> <li>Low efficiency</li> </ul>			
Hydrodesulfurization	<ul> <li>✓ Widely implemented method in the refining industry</li> </ul>	<ul> <li>Requiring significant energy to provide high P and T</li> </ul>			

Table 4 desulfurization techniques comparison [9], [12]–[15], [47], [55]–[57]

Desulfurization technique	Advantages	Disadvantages
	<ul> <li>✓ Effectively converts a wide range of sulfur compounds into hydrogen sulfide.</li> <li>✓ Low level sulfur product</li> <li>✓ Adaptable to various feedstocks</li> </ul>	<ul> <li>Less effective for complex compounds</li> <li>Production of H<sub>2</sub>S</li> </ul>
Electro-oxidation desulfurization	<ul> <li>Operates at mild conditions (T and P)</li> <li>No need for hydrogen</li> <li>High selectivity</li> <li>Low energy demand</li> <li>Promising in scaleup</li> <li>Applicable all phases (solid, liquid, or gas)</li> <li>High efficiency at low concentration</li> <li>No need to adding external oxidizing agents which cause corrosion and extra costs</li> </ul>	<ul> <li>Side reactions</li> <li>Dependent on the pollutant concentration (lower efficiency at high concentration)</li> </ul>

Each desulfurization method carries its unique set of advantages and limitations. Hydrodesulfurization (HDS) has been, so far, the top choice for removing sulfur from fuels in industrial site plants and many refineries already have the equipment for HDS, making it economical. However, HDS is highly energy demanding as it operates at high pressure and temperature condition, while electrochemical desulfurization techniques have the potential to

desulfurize components with consuming electrical energy and oxidize/reduce the sulfurous species at room temperature and pressure. Overall, electrochemical oxidation desulfurization has several benefits as mentioned in Table 4 with negligible drawbacks making it very interesting and promising for this application and motivates researchers to dedicate time and energy to develop this kind of electrochemical systems.

#### **1.4.** Objective of the current work

The objective of this research was to synthesize and characterize an efficient bimetallic electrocatalyst capable of electrooxidizing sulfur-containing organic pollutants. While there exist numerous studies on CoMo composites utilized as catalysts for hydrodesulfurization processes, none of them have explored the activity of this catalyst for the electrochemical oxidation of sulfurous species. Therefore, our aim was to develop CoMo bimetallic species deposited on a conductive carbonaceous support to catalyze electro-oxidation of organic pollutants.

We selected carbonaceous materials as the support, graphene and carbon nanotubes (CNT), due to their special electrical properties that facilitates electron transfer to electro-catalyst sites. Recognizing that these materials are generally inert and might lack strong interaction with CoMo species, we chose graphene oxide and carboxyl-functionalized CNTs (COOH-CNT) due to their oxygen-containing functional groups. The deposition of CoMo bimetallic species onto these functionalized carbonaceous supports was accomplished using a hydrothermal method.

Following the synthesis, various characterization techniques were employed to analyze the nanocomposite, including Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), Raman Spectroscopy, X-ray Photoelectron Spectroscopy (XPS), and Cyclic Voltammetry (CV). These techniques provided insights into the morphological, compositional, chemical, and electrochemical properties of the synthesized nanocomposite.

The electrocatalytic activity of the nanocomposites was evaluated using Methyl Orange (MO) as a model compound in cyclic voltammetry, chronoamperometry, and UV-vis spectroscopy. These assessments aimed to gauge the effectiveness of the synthesized nanocomposites in terms of their electrocatalytic capabilities.

#### 1.5. Thesis outline

The current thesis is comprised of the following chapters:

#### **Chapter 1: Introduction and Literature Review**

- Introduction to desulfurization processes.
- Brief overview of various desulfurization methods.
- Review of relevant literature, including key papers on desulfurization.
- Critical comparison of different desulfurization methods.
- Discussion on the objectives of the current research.

#### Chapter 2: Co-Mo catalysts on carbonaceous nanomaterials

- Explanation of the synthesis procedure for carbonaceous-supported CoMo.
- Detailed description of the methods used for characterization and evaluation of the synthesized nanocomposites.
- Presentation of results obtained from various characterization and evaluation tests: Raman Spectroscopy, Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), X-ray Photoelectron Spectroscopy (XPS), Cyclic Voltammetry (CV), Chronoamperometry, UV-vis Spectroscopy.
- Interpretation and discussion of the results obtained from each test or analysis.

#### Chapter 3: conclusions, contributions, and future recommendations

Highlighting the most important findings and recommendations for future works.

# Chapter 2. Co-Mo catalysts on

## carbonaceous nanomaterials

#### 2.1. Materials

Cobalt (II) nitrate hexahydrate ( $Co(NO_3)_2$ .  $6H_2O$ ) with 99.0% purity was employed as the cobalt precursor and sourced from SigmaAldrich. Anhydrous sodium molybdate  $(Na_2MoO_4)$  with a purity of 99.9% was purchased from SigmaAldrich and utilized as the molybdenum precursor. Graphitized multi-wall carbon nanotubes functionalized with carboxylate groups were obtained from cheaptubes, characterized by the properties listed in Table 5. Thioacetamide  $(CH_3CSNH_2)$ at 99.0% purity, acquired from SigmaAldrich, served as the reducing agent during the synthesis. A graphene oxide dispersion containing 0.4 wt% GO in water was sourced from Graphenea, detailed specifications provided in Table 6. For ink preparation, polyvinylidene fluoride (PVDF) with an average molecular weight ~534,000 g/mol, N-Methyl-2-pyrrolidone (NMP) with >99% purity, and ethylene glycol with 99.8% purity were all purchased from SigmaAldrich and used with the formulation explained in ink preparation section. Glass slides coated with Fluorine-doped tin oxide (FTO-glass) were utilized as the substrate for drop-casting the ink containing the synthesized nanoparticles. These slides were purchased from SigmaAldrich, featuring a surface resistivity of ~7  $\Omega$ /sq. The FTO glass slides were cut into 3 cm x 1.3 cm dimensions to function as the conductive substrate for the nanocomposite (electrocatalyst) ink. Sulfuric acid with an assay ranging between 95-98% purity was procured from ACP Chemicals and subsequently diluted to a 0.5 molar concentration using deionized water. This solution was utilized as the supporting electrolyte in electrochemical measurements. Additionally, methyl orange with a dye content of 85%, obtained from SigmaAldrich, was employed as the analyte in the electrochemical tests.
#### M.Sc. Thesis - Atefeh Shokrgozar; McMaster University - Chemical Engineering

Table 5 The most important properties for COOH-functionalized graphitized multi-walled carbon nanotubes reported by the manufacturer (cheaptubes.com)

Properties	Values
Outer Diameter	10-20 nm
Inside Diameter	3-5 nm
Ash	<0.1 wt%
Purity	>99.9 wt%
Length	10-30 μm
Specific Surface Area	100 m <sup>2</sup> /g
Electrical Conductivity	>100 S/cm
True density	$\sim 2.1 \text{ g/cm}^3$
COOH Content	1.53 wt%

Table 6 The most important properties for GO dispersion used in this research, reported by the manufacturer (Graphenea)

Properties	Values
Particle size (SEM)	D90: 5-7 μm, D50: 2-4 μm, D10: 1-2 μm
Color	Yellow-brown
Odor	Odorless
Dispersibility	Polar solvents
Solvents	Water
Concentration	4 mg/mL
рН	2.2-2.5
Monolayer content	(measured in 0.5 mg/mL) >95%
Elemental analysis	Carbon 49-56%
	Hydrogen 1-2%
	Nitrogen 0-1%
	Sulfur 2-3%
	Oxygen 41-50%

# 2.2. Devices used for preparations

Item	Device name	Manufacturer
1	Forced Air Oven	Cole-Parmer
5	Centrifuge	VWR
6	Magnetic stirrer with hot plate	Thermo Scientific
7	Analog Vortex Stirrer	VWR
8	Ultrasonic Bath	Bransonic
9	Ultrasonic Prob	QSonica
10	pH meter	Thermo Scientific

Table 7 List of laboratory devices used in catalyst preparation, ink and electrode preparation

# 2.3. Catalyst Preparation

Cobalt and molybdenum were synthesized on graphene oxide (GO) and multi-wall carbon nanotubes functionalized with carboxylate groups (hereafter referred to as CNT-COOH) using the hydrothermal technique, following a methodology similar to [58]. Three distinct catalyst grades were produced: CoMo-GO, CoMo-CNT-COOH, and CoMo-GO-CNT-COOH. To facilitate a comprehensive comparison among the three nanocomposites, all syntheses were designed to utilize an identical quantity of precursor salts, maintain consistent concentrations of functional groups provided by the supports, and employ an equal volume of solvent (deionized water) in the reaction environment. The detailed preparation procedures for these three nanocomposites were outlined as follows.

#### **2.3.1. CNT-supported Catalyst**

13.1 mg of graphitized multi-wall carbon nanotubes, already functionalized with acidic groups (referred to as CNT-COOH), were combined with 91.8 mg of cobalt (II) nitrate hexahydrate and 38.1 mg sodium molybdate dissolved in 40 mL deionized water. This resulting dispersion underwent sonication for 30 minutes using a probe sonicator (operating at 30% amplification, with a pulse of one second followed by a one-second pause) and was subsequently mixed with 120 mg of thioacetamide, serving as the reducing agent. Following this, the mixture underwent an additional 10 minutes of sonication using the same parameters as mentioned before. The resulting solution was then transferred to an autoclave for a thermal treatment at 180°C, maintained for a duration of 10 hours. After the thermal process, the autoclave was allowed to cool to room temperature. The resultant dispersion was then transferred to centrifuge tubes for centrifugation (at 4500 rpm) and washed repeatedly with deionized water until reaching a pH close to that of deionized water (~6). Finally, the resulting catalyst was dried at 85°C for 7 hours in the oven.

#### **2.3.2. GO-supported Catalyst**

7.5 mL of the 4 mg/mL graphene oxide dispersion in water and sourced from Graphenea (find detailed information in Table 6) (30 mg graphene oxide total<sup>5</sup>) was combined with cobalt and molybdenum precursors (91.8 mg of cobalt (II) nitrate hexahydrate and 38.1 mg sodium molybdate), dissolved in 32.5 mL of deionized water<sup>6</sup>. The subsequent steps mirrored the preparation procedure outlined in the previous section (CNT-supported Catalyst).

<sup>&</sup>lt;sup>5</sup> As already noted in section 2.3, the basis for the support was providing the same concentration of functions, rather than the same quantity of carbons

<sup>&</sup>lt;sup>6</sup> The basis of solvent was having 40 mL total water in all synthesis.

# 2.3.3. GO-CNT-supported Catalyst

To explore the impact of utilizing a blend of GO and CNT carbonaceous materials as the support for the CoMo catalyst, a combination of 6.55 mg CNTCOOH with 3.75 mL GO <sup>7</sup>dispersion (containing 0.4 wt% GO in water) was employed as the carbonaceous support. The aim was to provide an equal distribution of 50% support material via CNTCOOH and 50% via GO. Subsequently, 91.8 mg Cobalt (II) nitrate hexahydrate and 38.1 mg sodium molybdate were introduced to this carbonaceous support mixture and dissolved in 36.25 mL deionized water. The following steps were taken similarly to the procedure mentioned in the synthesis procedures of CNT-supported and GO-supported catalysts.

Figure 4 shows the autoclave used in this work and the product after the hydrothermal method and before washing. summarizes all the CoMo nanocomposites synthesized by hydrothermal method and studied in this research as the electrocatalyst.





Figure 4 photos of autoclave used for synthesis of nanocomposites and the product containing the nanoparticles of CoMo on the carbonaceous support and unreacted species (i.e. after synthesis and before washing)

<sup>&</sup>lt;sup>7</sup> The basis is providing 50% of support with GO and other 50% with CNTCOOH

Error! Not a valid bookmark self-reference. summarizes all the CoMo nanocomposites

synthesized by hydrothermal method and studied in this research as the electrocatalyst.

Nanocomposites	Description
CoMo-GO	Cobalt and molybdenum species synthesized on graphene oxide.
CoMo-CNTCOOH	Cobalt and molybdenum species synthesized on multi-wall carbon nanotubes
	functionalized by carboxylate groups.
CoMo-GO-	Cobalt and molybdenum species synthesized on a carbonous mixture containing
CNTCOOH	50% multi-wall carbon nanotubes functionalized by carboxylate groups and 50%
	graphene oxide.
СоМо-	A physical mixture of CoMo-GO and CoMo-CNTCOOH containing 50% of each
GO&CNTCOOH	the nanocomposites.

Table 8 The nanocomposites synthesized and investigated in this study.

# 2.4. Ink preparation

The ink preparation approach mentioned in [59]–[63] were tried and tailored to get a uniform stable ink. A 5 wt% PVDF solution was prepared by dissolving 1.03 g of PVDF in 20 mL of NMP overnight at a constant temperature of approximately 40 °C. This solution was consistently and gently stirred on a magnetic stirrer with a hot plate and used unchanged for all subsequent ink preparations. For each nanocomposite, 10 mg was thoroughly dispersed in 1.4 mL of ethylene glycol using bath sonication for 30 minutes. Following this, 0.6 mL of the prepared PVDF solution was added to the nanocomposite dispersion and thoroughly mixed using a vortex mixer. The resulting dispersion was utilized as the nanocomposite ink for the subsequent drop-casting step, where the nanocomposites were cast onto the FTO-glass (Fluorine-doped tin oxide glass), collectively serving as the working. Figure 5 shows the prepared ink and FTO glasses used in this work.



Figure 5 The prepared ink and the FTO glass slides before casting

# 2.5. Electrode preparation

A 2.5 cm x 1.3 cm (3.25 cm<sup>2</sup>) area of the conductive side of the FTO-glass surface was coated by applying 300  $\mu$ L of the ink, and subsequently, it was heated at a constant temperature of approximately 50 °C for approximately 7 hours to allow complete solvent evaporation.

Overall, 92  $\mu$ L/cm<sup>2</sup> ink was used in electrode preparation. The resulting electrode, covering this specified area, was utilized as the working electrode in the electrochemical tests. Figure 6 presents a series of drop-cast electrodes both before and after the drying process.



Figure 6 A set of drop-casted electrodes before and after evaporating the solvent and getting dried on hot plate at  $\sim$ 70 °C for  $\sim$ 7 hours.

#### 2.6. Catalyst Characterization

The synthesized nanocomposites underwent various characterization techniques: Raman Spectroscopy to analyze chemical bonds, Scanning Electron Microscopy (SEM) for morphological details, Energy-dispersive X-ray spectroscopy (EDX) for compositional information, and X-ray photoelectron spectroscopy (XPS) for elemental identification.

#### 2.6.1. Raman Spectroscopy

Raman spectra were collected with a Renishaw InVia Laser Raman spectrometer, using a 300-mW solid state continuous wave laser (532 nm, 1800 L/mm grating).

#### 2.6.2. SEM and EDX

SEM is widely used to investigate the material surface morphology and feature size. EDS is utilized for elemental analysis, enabling the identification and quantification of elements in a sample. The SEM and EDX were conducted by FEI Magellan 400 equipped with Oxford instruments EDX detector. Secondary electron images were taken in immersion mode using accelerating voltage of 2 keV, while EDX was conducted at accelerating voltage of 15keV in mapping mode. The samples were coated with 10 nm of platinum to reduce charging effects.

#### 2.6.3. XPS

XPS is a valuable technique providing surface information on the present elements, their chemical bonding states, and their oxidation states. The XPS tests were conducted by PHI Quantera II Scanning XPS Microprobe with X-ray source Al K- $\alpha$  (1486.6 eV), X-ray Beam Conditions 100u25W15KV and the following settings:

• Mode: Spectra

- Pass energy: 224 eV (survey), 112 eV (C), 26 eV (Zn, O)
- Step size: 0.8 eV (survey), 0.1 eV (all elements)
- Take-off angle: 450 (angle between analyzer axis and sample surface)
- Multipak software (ver. 9.5) is utilized for data analysis

#### 2.7. Electrochemical Measurements

Electrochemical tests, including cyclic voltammetry and chronoamperometry, were conducted using a Metrohm Autolab (PGSTAT204 type). These tests aimed to assess the electrochemical activity of the nanocomposites. A three-electrode configuration was employed for all measurements. A Metrohm Ag/AgCl saturated KCl electrode served as the reference, while a 40 cm annealed platinum wire (0.5 mm diameter, 99.95% metal basis from Alfa Aesar), shaped as a coil, functioned as the counter electrode.

A 0.5 molar sulfuric acid solution served as the supporting electrolyte, with methyl orange (MO) added as an analyte model to facilitate redox reactions. Cyclic voltammetry tests were conducted within the range of -1 to +1 V at various scan rates (0.2, 0.1, 0.001 V/s) both with and without the presence of the analyte in the supporting electrolyte. This comparison aimed to observe the nanocomposites' electrocatalytic behavior.

Chronoamperometry tests were carried out exclusively for the identified electrocatalyst (identified from the current-potential plot in cyclic voltammetry), maintained for 5 hours at a constant potential linked to the observed oxidative peak in the cyclic voltammetry test performed with the electrolyte containing 0.5 molar sulfuric acid and 10 ppm MO.

UV-vis spectroscopy (TECAN) measured the absorbance intensity before and after chronoamperometry. The difference in absorbance indicated the percentage of MO electro-degradation through electrocatalytic oxidation.

Figure 7 illustrates the electrochemical reactor during a cyclic voltammetry test using 0.5 molar sulfuric acid as the supporting electrolyte without the analyte. Figure 8 highlights one of the chronoamperometry tests conducted for 30 ppm MO dissolved in 0.5 M sulfuric acid.



Figure 7 The picture of the electrochemical reactor used in this work including three-electrode configuration including Ag/AgCl electrode as the reference electrode, platinum coiled wire as the counter electrode, and FTO glass slide coated with the synthesized nanocomposite as the working electrode.



Figure 8 The chronoamperometry test for a 30 ppm MO in 0.5 M sulfuric acid

#### **2.8.** Raman Spectroscopy

Figure 9 illustrates the Raman Spectra measured by irradiating the samples by a 532 nm wavelength laser at room temperature from 100 cm<sup>-1</sup> to 3200 cm<sup>-1</sup> for all the reactant species, carbonaceous supports and synthesized nanocomposites, including cobalt nitrate, sodium molybdate, and thioacetamide, Graphene oxide (GO), multi-walled carbon nanotubes with COOH functional groups (CNT-COOH), CoMo deposited on GO (CoMo-GO), CoMo on CNT-COOH (CoMo-CNT-COOH), and CoMo on the 50%-50% mixture of CNT-COOH and GO. The peaks appeared in each spectrum are associated with the vibration of a particular chemical bonding.

In the Raman spectrum of cobalt nitrate, solely one peak appeared at ~1052 cm<sup>-1</sup> and it can be ascribed to vibration of the nitrogen-oxygen bond in nitrate [64]. In the sodium molybdate spectrum, the peaks at ~299 cm<sup>-1</sup>, ~804 cm<sup>-1</sup>, and ~888 cm<sup>-1</sup> can be all associated with the vibrations of the oxygen-molybdenum bond [65]–[67]. The spectrum measured for thioacetamide

showed eight more obvious peaks at ~465 cm<sup>-1</sup>, ~711 cm<sup>-1</sup>, ~1030 cm<sup>-1</sup>, ~1294 cm<sup>-1</sup>, ~1400 cm<sup>-1</sup> , ~1465 cm<sup>-1</sup>, ~2906 cm<sup>-1</sup>, and ~3085 cm<sup>-1</sup>. The peak at ~465 cm<sup>-1</sup> can be assigned to nitrogencarbon-sulfur or carbon-sulfur bonds vibrations, while the peak at  $\sim$ 711 cm<sup>-1</sup> should originate from C=S and C-C bonds vibrations. The vibrations in CH<sub>3</sub> and NH<sub>2</sub> could create the corresponding peak at ~1030 cm<sup>-1</sup> and vibrations through NH<sub>2</sub>, C-C, C-S, N-C-S probably made the peak at ~1294 cm<sup>-1</sup>. Both of the peaks at ~1400 cm<sup>-1</sup> and ~1465 cm<sup>-1</sup> can be related to the responses from CH<sub>3</sub> and CN bonds [68], [69]. Besides, the peaks around 3000 cm<sup>-1</sup> can be assigned to the vibrations of the bonds CH and NH [70]. In the spectrum of f-CNT, the peaks appeared at 1341 cm<sup>-1</sup> and 1580 cm<sup>-1</sup> can be assigned to the vibrations of D (defect) and G (graphetic) bands on carbon nanotubes, respectively. The G bands are the ordered C-C/C=C bands organized in aromatic structure (sp<sup>2</sup> hybridization) and the D bands are the structural defects that exist on the surface of the tubes as C-O (sp<sup>3</sup>) and C=O (sp<sup>2</sup>). The C-O band originates from the carboxylic acid functional groups on the surface of tubes, while the C=O band can be associated with either carboxylic or carbonyl functional groups. The intensity of the peak related to G band is higher than that of D band, and thus the majority of the carbons are arranged in ordered aromatic structures without defects [71]-[73]. Moreover, a secondary D-band peak appeared for CNT-COOH at 2686 cm<sup>-1</sup> [74], [75]. The last peak in CNT-COOH at 2930 cm<sup>-1</sup> could account for C-H vibrations on both G and D bands (C=C and C-O).

Like CNT-COOH spectrum, that of GO includes two characteristic peaks at 1349 cm<sup>-1</sup> and 1594 cm<sup>-1</sup> correspond to D and G bands on graphene, respectively, and the concentration of D bands (defects) is lower than that of G bands. However, the stronger peaks in GO spectrum implies that there are fewer impurities in the GO compared to CNT-COOH. In GO spectrum the intensity of G band peak is higher than that of D band, while in CoMo-GO the concentration of D bands is higher

than that of G bands. This may indicate that during the synthesis reaction, more oxidative defects were formed on GO, likely because the thermal treatment caused the graphene edge carbons to oxidize. Additionally, the G band peak in the spectrum of CoMo-GO had a small shift to lower wave number (~1572). This shift can also be related to GO structure change from single layer to multi-layer or some minor aggregations [76]. There is another peak in CoMo-GO spectrum at ~930 cm<sup>-1</sup> which also appeared in the spectra of two other composites including CoMo-CNT-COOH and CoMo-GO-CNT-COOH and can be indicative of vibrations associated with Mo=O band [76]-[79]. This peak appeared with higher intensity for CoMo-GO compared to two other composites, indicating deposition of higher Mo sites on GO than CNT-COOH. The small peaks at ~815 cm<sup>-1</sup> and ~660 cm<sup>-1</sup> could be ascribed to Mo<sub>2</sub>O and Co<sub>3</sub>O<sub>4</sub>, respectively [76]–[82]. These peaks appeared with lower intensity for CoMo-GO compared to the similar peaks on CoMo-CNT-COOH spectrum. As the intensity of a peak can be interpreted as the concentration of that bond, the summation of the intensities of the peaks at 660, 815, and 930 cm<sup>-1</sup> can be considered as the total concentration of Co and Mo on the support. Accordingly, it can be concluded that in CoMo-CNT-COOH nanocomposite higher concentrations of Co and Mo were deposited compared to CoMo-GO. Therefore, this could be said that the interaction between the metals and CNT-COOH is stronger than that between the metals and GO surface.

All the D, G and 2D bands shifted to lower wavenumbers in CoMo-CNT-COOH compared to the pure CNT-COOH and it could be, similar to pure GO versus CoMo-GO, due to attraction forces between tubes causing aggregation. The spectrum of CoMo-GO-CNT-COOH has the same peaks as CoMo-GO and almost with the same intensity.



Figure 9 Raman spectra of cobalt nitrate, sodium molybdate, and thioacetamide, Graphene oxide (GO), multi-walled carbon nanotubes with COOH functional groups (CNT-COOH), CoMo deposited on GO (CoMo-GO), CoMo on CNT-COOH (CoMo-CNT-COOH), and CoMo on the 50%-50% mixture of CNT-COOH and GO.

# 2.9. Scanning Electron Microscopy (SEM)

Figure 10 illustrates the SEM images taken by secondary electrons, depicting the morphology of the synthesized nanocomposites and the histogram of particle size distribution. Individual particles



Figure 10 SEM images and particle size distribution for the synthesized nanocomposites CoMo-GO, CoMo-CNT-COOH, CoMo-GO-CNT-COOH

#### M.Sc. Thesis – Atefeh Shokrgozar; McMaster University - Chemical Engineering

shown in each image, not the clusters, were defined manually in ImageJ to obtain the average particle size (the red dotted circles show one of the particles in each image).

Image a, b, and c show CoMo spherical particles deposited on 2D sheets of GO, on nanotubes of carbon, and on both of these carbonaceous supports (GO and CNT) clearly. The SEM images reveal deposition of higher population of CoMo particles on CNT-COOH compared to GO. The majority of GO surfaces remained untouched as shown in CoMo-GO and CoMo-GO-CNT-COOH images. This observation is in agreement with the intensity of peaks relevant to Co and Mo in Raman Spectroscopy of CoMo-CNT-COOH and CoMo-GO nanocomposites, and it could be due to stronger attractive interaction between CoMo and CNT compared to GO. The aggregation of graphene sheets was also observed on the SEM image of CoMo-GO (image a). A few of these aggregations is shown in CoMo-GO SEM image with blue arrows.

Particle size is one of the important parameters in catalysts activity as catalysis is a surface phenomenon and the more  $\frac{Surface}{Volume}$  (=  $\frac{3}{R}$ ), the more area available for the species to react on and thus the more catalysis activity. This is thus anticipated that the composite with smaller catalyst particles deposited on the support would show higher electrocatalytic performance. The average particle size and particle size distribution diagram were obtained using ImageJ and the data are presented next to each image. The average particle size for CoMo particles deposited on GO (~25 particles), CNT-COOH (~75 particles), and the GO-CNT-COOH (~87 particles) mixture were measured 204 nm, 141nm, 127 nm, respectively, indicating deposition of smaller particles on CNT-COOH than GO. The probable higher interaction between CNT-COOH and CoMo (higher affinity) may have caused a higher number of primary nuclei of CoMo particles on CNT and since the metal content was limited, the final grown particles deposited on CNT were smaller than that of deposited on GO.

# 2.10. EDX

Energy-dispersive X-ray spectroscopy (EDX) for the three nanocomposites CoMo-GO, CoMo-CNT-COOH, CoMo-GO-CNT-COOH are presented in Figure 11, Figure 12, and Figure 13 respectively. Overall, the spectra confirmed presence of Co, Mo, S, O, and C in all the nanocomposites, indicating deposition of both sulfides and oxides of Co and Mo on carbonaceous supports (GO and CNT-COOH) as expected due to using thioacetamide as the reducing agent in the synthesis. The maps and they originate from the copper tape, and environmental contamination, respectively. for all the composites show a uniform distribution of the elements across the mapping area. It should be noted that the Cu and Ti peaks presented in the spectra do not belong to the sample, and they originate from the copper tape, and environmental contamination, respectively.



Figure 11 Energy Dispersive X-ray Scanning Spectroscopy (EDX) on mapping mode for CoMo-GO confirming the presence of Co, Mo, S, O, and C in CoMo-GO and the elements distribution across the area shown in the image.



Figure 13 Energy Dispersive X-ray Scanning Spectroscopy (EDX) on mapping mode for CoMo-CNT-COOH confirming the presence of Co, Mo, S, O, and C in CoMo-GO-CNT-COOH and the elements distribution across the area shown in the image.



Figure 12 Energy Dispersive X-ray Scanning Spectroscopy (EDX) on mapping mode for CoMo-GO-CNT-COOH confirming the presence of Co, Mo, S, O, and C in CoMo-CNT-COOH and the elements distribution across the area shown in the image.

Error! Not a valid bookmark self-reference. provides a comparison between composition of elements in the nanocomposites. The Co/Mo weight-base ratio in all samples is almost one, while in CoMo-CNT-COOH more Mo species were detected compared to Co and the initial weight ratio of Co/Mo in the synthesis environment was ~1.6 (equivalent to ~2.7 molar ratio). It could be concluded that Co has more affinity with GO than CNT-COOH. The compositions estimated for CoMo-GO-CNT-COOH are not a linear function of compositions for CoMo-GO and CoMo-CNT-COOH, but they show higher concentrations for S, Co, Mo. Accordingly, there could be some interactions between GO and CNT-COOH making a positive effect on the total interaction between the support and the elements S, Co, and Mo, leading to deposition of higher concentrations of S, Co, and Mo on the mixed support. Based on the elements detected in EDX, sulfides and oxides of Mo and Co were synthesized on the supports, while concentration of sulfide species is higher on CoMo-GO-CNT-COOH nanocomposite than CoMo-GO and CoMo-CNT-COOH. As the chemistry of GO and CNT is the same (same carbon structure and same population of functions), it seems that the geometry difference between GO and CNT plays a vital role in surface energy of the support and thus the interaction with the CoMo species, making formation of either sulfide or oxide more favorable.

Table 9 compositional information	gained by EDX	characterization tes	st for all three	nanocomposites,	including CoMo
GO, CoMo-CNT-COOH, CoMo-GO-CNT-C	OOH.				

Element	CoMo-GO Wt%	CoMo-CNT-COOH Wt%	CoMo-GO-CNT-COOH Wt%
С	8.36	8.02	3.93
0	22.28	21.36	10.47
S	32.91	32.94	38.21
Ti	0.67	0.40	2.48
Co	16.47	13.66	19.09
Cu	2.59	7.66	5.77
Мо	16.72	15.97	20.05
Total	100.00	100.00	100.00

#### 2.11. XPS

X-ray Photoelectron Spectroscopy (XPS) was utilized to examine the surface chemical properties of the carbonaceous supports (CNT-COOH and graphene oxide). Figure 14 shows scan survey spectra of CNT-COOH obtained by XPS test. The test was collected at three different points to see sample composition consistency. This sample showed mostly C peak along with very small O peak, revealing the CNT product used in this research had oxygen-containing functions but in a low concentration. Figure 15 shows C1s peak at 285 eV that could be the characteristic peak for C-C [83]–[85]. No peak appeared for oxidized carbon, confirming low degree of functions on the carbon nanotubes used in this work. However, SEM images and Raman spectra showed the highest amount of CoMo deposition on CNT and the lowest amount of deposition on GO. Comparing these two results reveals there probably were high degree of defects on CNTs.







Figure 15 carbon peaks in CNT-COOH XPS survey.

Figure 16 illustrates scan survey spectra for graphene oxide (GO) obtained by XPS test. The spectra were collected at three different points to see sample composition consistency. This sample showed strong C and O peaks along with small S peaks, indicating high concentration of oxygen-containing groups on graphene and presence of some sulfur elements (impurity which probably origin from treatment with sulfuric acid in functionalization procedure). Figure 17 illustrates three peaks at 284.74, 286.80, and 288.24 eV for C1s, indicating the presence of three types of carbon species which could be assigned to C-C, oxidized carbons, and C=O, respectively [83], [84], [86]. Therefore, the graphene oxide used in this research, unlike the f-CNT, had been highly oxidized. It was expected to observe a high load of CoMo particles deposited on GO, while SEM images did not meet this expectation, CoMo particles have higher affinity with CNTs than to GO.



Figure 16 XPS scan survey for graphene oxide



Figure 17 carbon peaks in GO XPS survey

Figure 18 presents scan survey spectra of CoMo-GO nanocomposite, collected at three different points. This sample showed elements of Co, Mo, O, C, and S. For all the element except molybdenum, the strongest photoelectron peak was selected as characteristic peak. As for

molybdenum, although the strongest peak was detected for Mo3d, it overlapped with S2s peak, and thus Mo3p was selected as representative of Mo in all the nanocomposites.



Figure 18 XPS scan survey for CoMo-GO

Figure 19 contains the characteristic peaks measured for C1s, S2p, Co2p3, and Mo3p3 in CoMo-GO nanocomposite. Three peaks were detected for C1s, including 284.74, 285.61, 286.97 eV, corresponding to C-C, C-O, and C=O, respectively [83], [84], [86], [87]. The S2p spectrum contains five characteristic peaks at 162.07, 163.33, 164.46, 168.81, and 170.03 eV, revealing presence of five sulfur-containing species. The peaks at 162.07 and 163.33 eV could be associated with S2p<sub>3/2</sub> and S2p<sub>1/2</sub> orbitals, associated to  $S^{2-}$  and  $S_2^{2-}$  in one phase like Mo-S<sub>x</sub>.[88], [89]. The peaks at 164.46, 168.81eV are attributed to S2p<sub>3/2</sub> and S2p<sub>1/2</sub> orbitals in another phase like Co-S<sub>x</sub> and the weaker peak at 170.03 eV can arise from partial oxidation of sulfur [90].

In Co2p spectrum, there are four peaks at 779.52, 781.36, 783.60, 786.60 eV. The peaks at 779.52, 781.36 eV are the primary peaks corresponding to Co-S and Co-O, while the other three peaks on the higher binding energy could be satellite peaks [89].

Mo3p3 showed three peaks at 395.51, 398.60, and 401.75 eV, indicating the presence of MoS2, MoO2, MoO3 [91]–[93].



Figure 19 Survey on S2p, Co2p, C1s, and Mo3p in CoMo-GO

Figure 20 presents survey spectra of CoMo-CNT-COOH conducted at three different points for composition consistency. This sample showed elements of Co, Mo, O, C, and S.



Figure 20 XPS scan survey for CoMo-CNT-COOH

Figure 21 shows the peaks measured for C1s, S2p, Co2p3, and Mo3p3 in CoMo-CNT-COOH nanocomposite. There are four peaks that appeared for carbon at 284.10, 284.80, 285.45, 286.91 eV, showing the presence of four carbon-containing bonds. These peaks origin from C–C, C-O, C=O, and O-C=O, respectively [83], [84], [86], [87]. The S2p, similar to what has been observed for CoMo-GO, showed five characteristic peaks at 162.03, 163.33, 164.63, 169.01, and 170.21 eV, corresponding to  $S^{2-}$  and  $S_2^{2-}$  in Mo-S<sub>x</sub>,  $S^{2-}$  and  $S_2^{2-}$  in Co-S<sub>x</sub>, and partial oxidation of sulfur[88]–[90]. Four peaks appeared for Co2p3 at 779.55 (Co-S), 781.30 (Co-O), 783.44 (satellite peak), 786.45 eV (satellite peak) [89], that are identical to the peaks measured for CoMo-GO. Furthermore, the three peaks detected for Mo3p3 were at the same binding energy mentioned for CoMo-GO, including 395.29, 398.54, 401.96 eV associated with MoS<sub>2</sub>, MoO<sub>2</sub>, MoO<sub>3</sub>, respectively [91]–[93].

Figure 22 displays the survey spectra obtained for CoMo-GO-CNT-COOH (at three different locations), confirming presence of Co, Mo, O, C, and S in this nanocomposite.



Figure 21 C1s, S2p, Co2p3, and Mo3p3 peaks in CoMo-CNT-COOH spectrum





Figure 22 XPS survey for CoMo-GO-CNT-COOH

Figure 23 shows the peaks measured for C1s, S2p, Co2p3, and Mo3p3 in CoMo-GO-CNT-COOH nanocomposite. There are two peaks that appeared for carbon at 284.78 and 285.96 eV, showing the presence of two carbon-containing bonds including C-C and C-O, respectively [83], [84], [86], [87]. S2p, Co2p3, and Mo3p3 peaks are similar to those described for CoMo-GO and CoMo-CNT-COOH.



Figure 23 C1s, S2p, Co2p3, and Mo3p3 peaks in CoMo-GO-CNT-COOH spectrum

To sum up, XPS results confirmed that hydrothermal approach deposited different oxides and sulfides of Co and Mo on partially oxidized CNT and GO. Considering the area under the peaks as the species concentration, for CoMo-CNT-COOH, Co sulfide is the dominant Co species, while Mo dioxide and then Mo disulfide account for the majority of molybdenum species deposited on CNT-COOH. In CoMo-GO, Co sulfide is the main cobalt-containing species, while Mo dioxide and disulfide are closely competing as the main Mo-containing species deposited on GO. Whereas,

in CoMo-GO-CNT-COOH, the dominant species are Cobalt sulfides and Molybdenum sulfides. The scan survey on GO showed a small sulfur peak and this sulfur could be an extra sulfur source in CoMo-GO and CoMo-GO-CNT-COOH composites. As discussed before in EDS, despite the same chemistry in GO and CNT, the geometry is different, and it affects their surface energy and thus their interaction with the particles. Accordingly, thermodynamics decides on which chemical structure of CoMo is more stable (thermodynamically favorable) on the support.

Besides, as expected, XPS did not detect formation of chemical bonding between Co, Mo and the carbon and thus CoMo were deposited on the CNT and GO with physical interactions.

#### 2.12. Cyclic Voltammetry

Cyclic voltammetry (CV) is perhaps the most popular electrochemical characterization technique for the assessment of the oxidation and reduction of species (electron-initiated chemical reactions) and thus CV plays very important role in studying and evaluating performance of electrocatalysts. The voltage difference between the working electrode and reference electrode is swept linearly in time, starting from a particular voltage (V<sub>1</sub>) to a maximum amount and then decreasing to another voltage (V<sub>2</sub>) and recording the working electrode current as the response function. Interpreting the CV plot provides information about the electrochemical changes happening at the electrolyteelectrode interface [94]. In the current work, CV test for 0.5 molar sulfuric acid without analyte and for 0.5 molar sulfuric acid containing 10 ppm methyl orange as the analyte model were performed.

## 2.12.1. Cyclic Voltammetry in supporting electrolyte

Figure 24 illustrate the working electrode cyclic voltammetry (hereafter CV) plots obtained by varying voltage from -1 V to +1 V with 0.2 V/s rate and measuring the produced current as the

response signal. As explained in the previous chapter (in electrochemical tests section), all the electrochemical tests were carried out using three electrodes including platinum coil as the counter electrode, Ag/AgCl reference electrode, and different working electrodes (GO, CNT-COOH, CoMo-GO, CoMo-CNT-COOH, CoMo-GO-CNT-COOH, CoMo-GO&CNT-COOH). A 100 mL 0.5 M sulfuric acid was used as the electrolyte in these set of cyclic tests (no analyte). The purpose of using 0.5 M sulfuric acid is to provide high ionic conductivity to facilitate ions transfer from bulk of solution to the surface of electrodes, where the ions are reduced or oxidized at cathode or anode electrode respectively.

The electrodes made of CNT-COOH, GO, CoMo-GO showed oxidative peak which cannot originate from oxidation of sulfuric acid (already at highest possible oxidation state), and thus they may be related to oxidizing some carbons on CNTs and GO to sulfonated carbons (functionalizing with -SO<sub>3</sub> H and releasing O<sub>2</sub> on the working electrode and/or functionalizing the carbon sites with -O- SO<sub>3</sub> H group). Figure 25 displays GO and sulfonated GO structures schematically, to visualize this possible occurrence on the carbonaceous materials.

Comparing the current produced by the working electrodes in CV test, the electrode made of CoMo-CNT-COOH exhibited substantially lower resistance, producing  $\sim$ 0.03 A at 1 V in oxidation curve and  $\sim$ -0.045 A at -1 V in reduction section. The second highest reduction current was produced by the CoMo-GO-CNT-COOH electrode (-0.022 A), and then by GO and CoMo-GO electrodes ( $\sim$  -0.02 A) at -1V.

Comparing the CV plots CoMo-GO-CNT-COOH, CoMo-GO&CNT-COOH (50%-50% physical mixture of CoMo-GO and CoMo-CNT-COOH), CoMo-GO and CoMo-CNT-COOH reveals that CNT-COOH is more efficient support for CoMo than GO, since GO-containing composites showed high resistance and very low current in CV test. Therefore, electrode conductivity for all

the electrodes except CoMo-CNT-COOH acts as a limiting step and reduces the overall electrochemical efficiency.

In addition, comparing the plots illustrates synthesizing CoMo on a mixture of the carbonaceous supports nor mixing CoMo-GO and CoMo-CNT-COOH physically could improve the electrode conductivity as both of them produced a significantly lower current than CoMo-CNT-COOH, (The composite of CoMo-GO-CNT-COOH produced -0.022 A at -1 V and the physical mixture made ~0 in the voltage range). Although GO showed slightly higher conductivity than CNT-COOH, CoMo-CNT-COOH showed remarkably higher conductivity than CoMo-GO, and thus CNT outperforms when playing the role of support material for electrocatalysts.



Figure 24 cyclic voltammetry plots with 0.2 V/s scan rate in three-electrode configuration, including platinum coil as the counter electrode, Ag/AgCl reference electrode, and different working electrodes (GO, CNT-COOH, CoMo-GO, CoMo-CNT-COOH, CoMo-GO-CNT-COOH, CoMo-GO&fCN conducted in a 0.5 molar sulfuric acid solution as electrolyte



Figure 25 Schematic picture of GO, and sulfonated GO structures, adapted from [95]

#### 2.12.2. Cyclic Voltammetry in analyte

Figure 26 demonstrates the CV tests results for CNT-COOH, GO, CoMo-GO, CoMo-CNT-COOH, CoMo-GO-CNT-COOH, and CoMo-GO&CNT-COOH conducted for a 100 mL 0.5 molar sulfuric acid solution containing 10 ppm Methyl Orange (MO) to learn which composite can electrocatalytically oxidize MO molecules. The working electrode made of CoMo-CNT-COOH exhibited two oxidation peaks at -0.4 V (0.003 A) and 0.58 V (0.001 A), whereas there were no peaks in CV plot of this nanocomposite in the CV test conducted in 0.5 molar sulfuric without MO. Therefor, the appeared peaks in **Error! Reference source not found.** are associated with oxidation of MO and revealing production of two products one at -0.4 V and another at 0.58 V. As the intensity of the first oxidation peak is approximately four times higher than that of the second oxidation peak, the chronoamperometry test was carried out at constant voltage -0.4 V. In this condition, the Co and Mo sites are probably reduced from a higher valance state to a lower valance state (like  $Co^{3+}$  to  $Co^{2+}$ , and  $Mo^{+6}$  to  $Mo^{+4}$ ), oxidizing MO molecules while protons and lowvalence metal ions are reduced to hydrogen molecules and higher-valence ions at the counter electrode (cathode) [47]. It is estimated that at the first oxidative peak (at -0.4 V), the N=N bond gets oxidized and at the second peak (at 0.58 V) the aromatic ring gets oxidized. This could be supported by UV-vis spectroscopy and comparing the spectra before and after degradation at constant voltage, but the available UV-vis cannot measure the light absorbance at low wavelength (the absorbance of aromatic ring is in range of 200-300 nm).

The results show no electrocatalytic activity for CoMo-GO, CoMo-GO-CNT-COOH, and CoMo-GO&CNT-COOH in the presence of MO, so none of them could reduce or oxidize MO molecules. The test was also conducted for CNT-COOH and GO as control measurements and the findings revealed a very small oxidation peak at the same location of the first oxidation peak of CoMo-CNT-COOH (i.e. -0.4 V), confirming the electrocatalytic role of CoMo sites in CoMo-CNT-COOH. The current in electrochemical reaction is directly related to the rate of the reaction. Accordingly, it can be predicted that as the current at the oxidative peak of CoMo-CNT-COOH is 12 times higher than that of CNT-COOH, the degradation rate of MO by CoMo-CNT-COOH could be up to 12 times faster than that of CNT-COOH.



Figure 26 Cyclic voltammetry tests with 0.2 V/s scan rate in three-electrode configuration, including platinum coil as the counter electrode, Ag/AgCl reference electrode, and different working electrodes (GO, CNT-COOH, CoMo-GO, CoMo-CNT-COOH, CoMo-GO-CNT-COOH, CoMo-GO&CNT-COOH) conducted for a 100 mL 0.5 molar sulfuric acid solution containing 10 ppm Methyl Orange (MO)

## 2.13. Chronoamperometry

Chronoamperometry technique is a common electrochemical test applying a constant voltage to see the stability of the electrochemical system while sampling the solution and measuring the light absorbance by UV-vis spectroscopy can be used to estimate MO degradation percentage.

The test was conducted for 5 hours (18,000 s) with applying constant -0.4 V to the anode consisting of FTO-glass coated by CoMo-CNT-COOH and different initial MO concentrations of 10, 20, 30, and 40 ppm. The current was measured during the test through a three-electrode configuration and the obtained data are presented in Figure 27. Overall, the current in the figures for 10, 20 and 30

#### M.Sc. Thesis - Atefeh Shokrgozar; McMaster University - Chemical Engineering

ppm are stable with time, indicating the catalyst, electrode, and electrolyte are functioning in steady sate condition, indicating a steady state degradation of MO. However, the chronoamperometry results for 40 ppm is less stable compared to other figures, reaching a plateau of approximately 15000 s (~4 h) after starting the test.

The current increased 1.2 times from -6e-5 A (-0.06 mA) to -7e-5 A (-0.07 mA) by increasing the MO initial concentration from 10 ppm to 20 ppm. The current then increased ~18 times from -7E-5 A (-0.07 mA) to 13E-4 (1.3 mA), while the concentration increased from 20 to 30 ppm. On the other hand, there was a 0.9-times depletion of the current when the initial MO concentration elevated for another 10 ppm from 30 ppm to 40 ppm. As the current is representative of the electrochemical reaction rate (transferred charge per second), it could be concluded that the CoMo-CNT-COOH electrocatalyst provided the fastest electrooxidation process for the solution containing 30 ppm MO as compared to the initial concentration. The MO molecular diffusion from the bulk electrolyte to the anode surface and the diffusion of degraded molecules from the anode surface to the bulk are the limiting (controlling) steps for low and high MO concentrations, respectively. There could be insufficient numbers of molecules available in the vicinity of the anode to be oxidized at low MO concentration and, on the other hand, the diffusion coefficient of the products may be too small at high MO concentration, making desorption of products from electrocatalytic sites and diffusion of them to the bulk of solution more difficult.



Figure 27 Chronoamperometry test results conducted by applying constant -0.4 V potential on CoMo-CNT-COOH electrode for 5 hours in 100 mL of 10, 20, 30, and 40 ppm MO in 0.5 molar sulfuric acid electrolyte.

## 2.14. UV-vis Spectroscopy

The light absorbance changes (at  $\lambda_{max}$ =507 nm) before and after the chronoamperometry test (applying constant voltage -0.4 V for 5 hours to a 100 mL solution containing 0.5 molar sulfuric acid and MO with different initial concentrations 10, 20, 30, and 40 ppm) used to quantify the MO degradation. As presented in **Error! Reference source not found.**, the MO degradation values for the MO solutions with C<sub>0</sub> equal to 10, 20, 30, and 40 ppm were estimated to be 18%, 23%, 67%, and 23%, respectively. As expected from the chronoamperometry results, the 30 ppm solution experienced the highest dye removal and fastest kinetic (highest dye concentration change over
the same period of time as other solutions). The reason for this maximum degradation was hypothesized in previous section.



Figure 28 UV-vis spectra for electrolyte solution containing MO before and after 5-hour electrooxidation by CoMo-CNT-COOH at -0.4 V conducted for different initial MO concentration of 10, 20, 30, and 40 ppm with 100 mL volume.

# **Chapter 3. Significant Contribution and**

## Recommendations

#### 3.1. Key findings and contributions

In conclusion, the thorough application of various characterization techniques has illuminated the structural, morphological, elemental, and electrochemical properties of the synthesized nanocomposites. The successful deposition of sulfides and oxides of Co and Mo on carbonaceous supports (GO and CNT-COOH) via the hydrothermal synthesis route was evident from the EDX and XPS analysis.

Based on the detailed findings and discussions presented in the third chapter regarding different characterizations including Raman Spectroscopy, Scanning Electron Microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX), Cyclic Voltammetry (CV), Chronoamperometry, and UV-vis Spectroscopy, the following conclusions can be drawn:

• Raman Spectroscopy Analysis:

The Raman spectra of different materials (cobalt nitrate, sodium molybdate, thioacetamide, Graphene oxide, multi-walled carbon nanotubes with COOH functional groups, CoMo deposited on GO and CNT-COOH, and their mixtures) revealed distinct peaks associated with specific chemical bonds, indicating the structural characteristics of the synthesized nanocomposites.

The intensity and position of Raman peaks provided insights into the interactions between metal species (Co and Mo) and carbonaceous supports (GO and CNT-COOH). This analysis suggested stronger interactions between metals and CNT-COOH compared to GO, affecting the deposition concentration of Co and Mo on these supports.

• SEM and EDX Analysis:

SEM images showed the morphology of synthesized nanocomposites and revealed loading higher concentration of CoMo on CNT-COOH with smaller average particle size, compared to GO.

EDX analysis confirmed the presence of Co, Mo, S, O, and C in all nanocomposites, with variations in the concentrations based on the support material, indicating successful deposition of sulfides and oxides of Co and Mo on carbonaceous supports.

• XPS analysis:

XPS results confirmed the existence of carbon, oxygen, sulfur, cobalt, and molybdenum in all the synthesized nanocomposites. Cobalt sulfide emerged as the dominant cobalt species in CoMo-CNT-COOH, whereas molybdenum dioxide and disulfide were the primary molybdenum species. CoMo-GO showcased Co sulfide as the main cobalt species, while molybdenum dioxide and disulfide closely competed as the primary molybdenum species. In CoMo-GO-CNT-COOH, the prevalent species were cobalt sulfides and molybdenum sulfides.

• Cyclic Voltammetry and Chronoamperometry Analysis:

Cyclic Voltammetry tests demonstrated the potential electrocatalytic activity of CoMo-CNT-COOH for MO molecules through electro-oxidation process.

Chronoamperometry results indicated the stability of CoMo-CNT-COOH during the 5-hour batch test at constant -0.4 V in Methyl Orange degradation. Higher current was produced in chronoamperometry test conducted for a MO solution with initial concentration of 30 ppm, and lower current for higher and lower initial concentrations.

• UV-vis Spectroscopy Analysis:

UV-vis spectroscopy quantified the degradation of Methyl Orange, highlighting the CoMo-CNT-COOH catalyst's capability to effectively degrade MO, with the highest efficiency observed at 30 ppm initial MO concentration.

Overall, the comprehensive characterization techniques employed in this study provided valuable insights into the structural, morphological, elemental, and electrochemical properties of the synthesized nanocomposites. The results suggest that CoMo-CNT-COOH exhibited promising electrocatalytic activity for MO degradation, indicating its potential application in environmental remediation. Moreover, the varying behavior observed in different concentrations of MO emphasizes the importance of understanding diffusion limitations for optimizing the electrooxidation process. These findings contribute to the understanding of nanocomposite behavior and pave the way for further research in the development of efficient catalysts for pollutant degradation.

#### **3.2 Recommendations and Future Works**

Optimization of Synthesis Conditions: Further exploration and fine-tuning of the hydrothermal synthesis parameters (temperature, pressure, duration, etc.) can be conducted to enhance the deposition efficiency and control the morphology of the nanocomposites. This optimization could potentially lead to improved catalytic performance. It is expected to end up with smaller particles if the reaction occurs at shorter time.

Exploration of Hybrid Nanocomposites: Exploring the feasibility of hybrid nanocomposites by incorporating other nanomaterials or altering the composition ratios of GO, CNT-COOH, Co, and Mo could offer novel catalytic properties and broaden the application scope in various electrochemical processes.

66

Investigation and understanding the difference in electrocatalytic activity of CoMo sulfides and CoMo oxides.

Long-Term Stability and Durability Studies: Evaluating the long-term stability and durability of the synthesized nanocomposites under continuous electrocatalytic conditions is crucial for assessing their practical viability and lifespan, especially in industrial or environmental applications.

Exploration of Other Pollutant Degradation: Expanding the scope of pollutant degradation studies beyond Methyl Orange to various other organic pollutants (like thiophene (Th), benzothiophene (BT) or dibenzothiophene (DBT)) would help assess the versatility and applicability of the nanocomposites in diverse wastewater treatment scenarios. It is necessary to consider proper safety regulations during the experiments.

Studying electrocatalytic kinetics and reaction mechanisms through in-situ characterizations, such as employing techniques like NMR (Nuclear Magnetic Resonance), could offer valuable insights into potential rate-limiting steps and aid in designing more efficient catalysts.

67

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