

UNIVERSITY OF THE WITWATERSRAND

SCHOOL OF CHEMISTRY



A dissertation submitted to the Faculty of Science, University of the Witwatersrand, Johannesburg, in completion for the degree of Master of Science in Chemistry

Synthesis of platinum-based electrocatalysts using nitrogen doped onion-like carbon and WS₂ composites as the support for electrooxidation of ethanol in direct alcohol fuel cells

Author: Laercia Bila

Student number: 1623552

Supervisors: Dr. Siziwe Gqoba and Dr. Manoko Maubane-Nkadimeng

Declaration

I, Laercia Rose Bila, hereby declare that this dissertation which is submitted for a degree of Master of Science in the Faculty of Science, School of Chemistry, University of the Witwatersrand represents my original work, conducted under the guidance of Dr. Maubane-Nkadameng and Dr. Gqoba, and that all sources used or referred to have been properly cited and acknowledged. I affirm that this work has not been submitted elsewhere for any degree or examination. I take full responsibility for the accuracy and integrity of the content presented herein.



Laercia Bila

01/10/2024

Date



Dr. Maubane-Nkadameng

01/10/2024

Date



Dr. Siziwe Gqoba

01/10/2024

Date

Dedication

This study is a heartfelt devotion to my siblings:

My younger brother Junior Bila, my younger sister Carla Bila, and my older sister Thuli
Sithole.

Proverbs 17:17 “Friends love through all kinds of weather, and families stick together in all
kinds of trouble”.

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Presentations and awards

Presentations

- Authors: Laercia Bila, Ludwe Sikeyi, Zakhele Ndala, Avuya Gqoba, Siziwe Gqoba, Manoko Maubane-Nkadimeng
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Award(s)

- Won 5th prize (4th runner up): MSc Poster Presentation, University of the Witwatersrand
- Won third prize for flash talk and poster presentation: 6th International Symposium on electrochemistry.
- Won third prize for MSc presentation: 9th Collaboration Symposium.

Abstract

The study reports on the synthesis of onion-like carbons (OLCs)/tungsten disulfide (WS_2) composites as catalyst support for direct alcohol fuel cells (DAFC). OLCs were synthesized using waste engine oil over a flame pyrolysis (FP) method. The pristine OLCs (p-OLCs) were functionalized and purified using nitric acid (HNO_3). The functionalized OLCs (F-OLCs) were further doped with nitrogen using melamine to increase the electronic properties of the OLCs. WS_2 was synthesized using the colloidal method and oleylamine was used as the capping agent. Pt/p-OLCs, Pt/F-OLCs, and Pt/N-OLCs were synthesized using a reflux method where ethylene glycol was the reducing agent. Finally, WS_2 /N-OLCs were synthesized using the colloidal method and then Pt was dispersed on WS_2 /N-OLCs to form Pt/ WS_2 /N-OLCs.

High-resolution transmission electron microscopy showed the presence of onion-like rings in the OLCs and the quasi-spherical morphology, while a flower-like morphology was observed for WS_2 . Powder X-ray diffraction revealed that the synthesized WS_2 had traces of WO_3 due to the oxidation of WS_2 which introduces WO_3 impurities. Energy Dispersive X-ray Spectroscopy revealed that the OLCs derived from waste engine oil present some impurities that were attributed to the motor wear as well as the fuel. When Pt was loaded onto the WS_2 /N-OLCs composite, the WS_2 lost its original nanoflower morphology, which was attributed to the presence ethylene glycol used as a reducing agent. X-ray photon spectroscopy confirmed the successful synthesis of the Pt electrocatalysts.

Cyclic voltammetry was used to determine the oxidation of ethanol and the current density of the synthesized electrocatalysts. Interestingly, the Pt/p-OLCs electrocatalyst had a higher current density compared to Pt/F-OLCs and Pt/N-OLCs. This was attributed to metal impurities found in p-OLCs, which were reduced during the purification process. The Pt/ WS_2 /N-OLCs electrocatalyst showed higher current density compared to Pt/ WS_2 but this was low compared to Pt/N-OLCs. The data reveals that the addition WS_2 shows a co-catalyst behaviour, rather than a support.

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List of abbreviations

BCP – Brass collecting plate.

BET – Brunauer - Emmette - Teller

CNDs – Carbon nanodots

CVD – Chemical vapour deposition

CV – Cyclic voltammetry

DAFCs – Direct alcohol fuel cells

DEFCs – Direct ethanol fuel cells

EDS – Energy dispersive X-ray spectroscopy

EDLC - Electric double layer capacitors

EG – Encapsulated graphitized carbon

EOR – Ethanol oxidation reaction

EtOH – Ethanol

fCNDs – functionalized carbon nanodots

F-OLCs – Functionalized onion – like carbons

FP - Flame pyrolysis

FTIR – Fourier transform infrared spectroscopy

GCE – Glassy carbon electrode

HER – Hydrogen evolution reaction

HR-TEM – High resolution transmission electron microscopy

MWCNTs – Multiwalled carbon nanotubes

MWNTs – Multiwalled nanotubes

NC – Nitrogen doped carbon

N-OLCs – Nitrogen doped onion-like carbons

OER – Oxygen evolution reaction

OLA - Oleylamine

OLCs – Onion-like carbons

ORR – Oxygen reduction reaction

PEMFCs – Polymer electrolyte fuel cells

p-OLCs – Pristine onion – like carbons

PXRD – Powder X-ray diffraction

SEM – Scanning electron microscopy

SOFCs – Solid oxide fuel cell

SWCNTs – Single walled carbon nanotubes

TiO₂ – Titanium dioxide

TEM – Transmission electron spectroscopy

TGA – Thermogravimetric analysis

TMDs – Transition metal dichalcogenides

XPS – X-ray photon spectroscopy

XRD – X-ray diffraction

Outline of dissertation

Chapter 1: The introductory chapter, which describes the problem statement and motivation for this study, further outlines the research aims and objectives.

Chapter 2: The literature review expands on the first chapter, delving into the concepts covered in this study.

Chapter 3: This chapter provides a detailed description of the characterization techniques used in this study.

Chapter 4: This chapter discusses and interprets the results obtained from synthesizing doping and functionalizing onion-like carbons derived from waste engine oil.

Chapter 5: This chapter depicts and explains the synthesis of WS₂ using the colloidal synthesis method, and further elaborates on the characterization of the material.

Chapter 6: Presents the synthesis of Pt/p-OLCs, Pt/F-OLCs, and Pt/N-OLCs. This chapter also includes a detailed description of the characterization of Pt/p-OLCs, Pt/FOLCs, and Pt/NOLCs, along with cyclic voltammetry analysis.

Chapter 7: This chapter focuses on the synthesis, characterization, and application of Pt/WS₂/N-OLCs for ethanol fuel oxidation.

Chapter 8: Conclusions and relevant recommendations.

Appendix: This section has supplementary data attached for Chapter 4, Chapter 6, and Chapter 7.

Chapter 1: Introduction to the study

1. Background

1.1 Fuel Cells

Fuel cells are devices that convert chemical energy into electrical energy, offering improved energy efficiency compared to combustion Carnot engines. This process results in cleaner power generation from chemicals, contributing to a safer and more environmentally friendly outcome [1]. Fuel cells are applied in static or distribution of electrical generation, vehicle power, portable electricity production, and secondary power production [2]. Notably, direct alcohol fuel cells (DAFCs), a crucial component in transportation and portable electronic devices, have garnered significant attention. DAFCs, utilizing various alcohols as fuel, commonly opt for methanol and ethanol due to their straightforward operation and the ability to use these alcohols without a reformer [3]. Ethanol stands out as a preferred fuel source owing to its renewability, wide availability, and absence of harmful effects associated with methanol [4]. In contrast, methanol is considered a toxic fuel that can lead to permanent blindness or optic nerve damage if excessively inhaled [5]. In the electrochemical process, the anode oxidizes the fuel without generating pollutants, while the cathode reduces the oxidant [6]. Direct ethanol fuel cells use ethanol as the fuel source [4]. Although alcohol oxidation is generally slow, polymer electrolyte fuel cells (PEMFCs) exhibit superior electronic conduction compared to direct alcohol fuel cells with a similar electroactive site [7]. Several fuel cells have been studied in recent years and they include (i) direct alkaline fuel cells [8], (ii) solid oxide fuel cell (SOFC) [9], (iii) polymer electrolyte fuel cell (PEFC) [8], [9] (iv) phosphoric acid fuel cell [10], and molten carbonate fuel cell [11].

1.2 Nanocarbons

Carbon, a plentiful substance on earth, has captivated the interest of researchers for years [12]. Found on the periodic table, carbon is a versatile chemical element capable of forming various bonds and stable configurations with itself and a diverse array of elements [13]. Its orbitals can hybridize into sp , sp^2 , and sp^3 arrangements, paving the way for the existence of numerous carbon allotropes [13]. These allotropes emerge when carbon atoms covalently bond with one another based on their valence [14], forming one, two, or three bonds, respectively. While chemically akin, carbon allotropes exhibit distinct physical properties [14]. Among the naturally occurring allotropes are diamond, amorphous carbon, and graphite as shown in Figure 1.1, while synthetic processes have yielded an expanded array including graphene, carbon nanotubes, carbon nano-onions, fullerenes, carbon nano-horns, and nano-diamonds [15]. Carbon nanomaterials find diverse applications in electrochemical energy storage, biomedical fields, nanotechnology, electronics, and beyond [14], [16], [17].

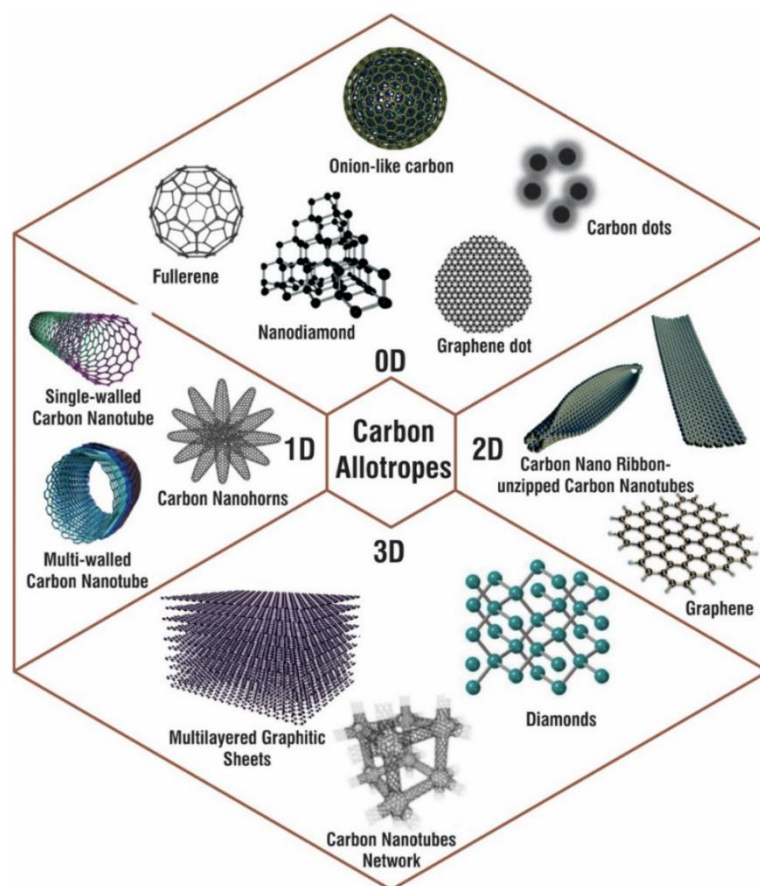


Figure 1.1: Carbon nanomaterials adapted from Gaur *et al.*, [18].

1.3 Problem statement

Fuel cells pose increased volumetric and gravimetric performance, reduced chemical and heat emissions, low maintenance, fuel versatility, and no generation of pollutants [2]. They are a better alternative to internal combustion engines, power plants and combustion Carnot engines due to the improvement of the overall efficiency in a smaller system and reduced environmental ramifications [19]. Despite the potential advantages, direct ethanol fuel cells face challenges such as sluggish oxidation mechanisms at the anode, deficient oxidation processes, ethanol crossover, expensive cell apparatus, catalyst deactivation by reaction intermediates, catalyst stability, and difficulty in controlling water and heat [20]. The total ethanol oxidation to CO_2 involves the release of 12 electrons for each ethanol molecule, breaking carbon bonds, and increased adsorption of intermediate compounds that pose a threat to platinum-based catalysts, making ethanol oxidation more challenging than methanol [3]. While platinum is recognized as a suitable electrocatalyst for direct ethanol fuel cells due to its exceptional properties, its applications are constrained by two main issues: poisoning of the Pt-based electrocatalyst leading to reduced catalytic activity and the controlled quantity of platinum due to increased costs [20]. To remedy this problem, research has focused on incorporating support materials such as silicon carbide, titanium dioxide, tungsten oxide, iridium oxide, and tin oxide [21]. Carbon supports such as carbon black, carbon nanotubes, onion-like carbon and graphene have also been reported [21]. While enhancement in catalytic activity has been reported with the carbon supports, the presence of carbon affects aspects such as mass transport, electronic conductivity, electrochemical active area, and operational stability which remains a major drawback of carbon-based electrocatalysts [22]. Therefore, it becomes crucial to design high-performance electrocatalysts for the electrocatalytic oxidation of ethanol in basic media and optimize the Pt loading on these electrocatalysts. In this study, a composite of tungsten disulfide with nitrogen doped onion-like carbons ($\text{WS}_2/\text{N-OLCs}$) was used as a support material for Pt-based catalysts. N-doped carbon is reported to have nitrogen atoms which are integrated into the carbon framework and contribute extra lone pairs of electrons [21]. This integration could ease the electron transfer from carbon to oxygen, thereby potentially improving the electronic characteristics of the carbon materials and WS_2 is a layered material that brings optical, chemical, catalytic, and electronic properties [23].

1.4 Motivation for the study

This research builds upon previous and ongoing studies aimed at enhancing Pt-based electrocatalysts for direct ethanol fuel cells (DEFCs). The primary focus is on designing electrocatalysts with improved performance while simultaneously reducing and optimizing the Pt loading. This reduction in Pt loading is crucial to minimize the risk of Pt poisoning in the electrocatalyst. Carbon-based materials, and transition metal dichalcogenides have demonstrated key properties essential for serving as catalyst support materials. These properties include the ability to conduct electricity, a higher surface area, and the capacity to maintain stability during the ethanol oxidation reaction (EOR). The core objective of this project is to leverage the unique properties of carbon-based nanomaterials (i.e., OLCs), and transition metal dichalcogenides (i.e., WS₂) in synthesizing Pt-loaded heteroatom-doped carbon nanomaterials. These materials will be employed as electrocatalysts for ethanol oxidation reactions in DEFCs. The underlying motivation for this study is to develop highly efficient Pt-based electrocatalysts with reduced Pt loading for DEFCs. The intention is to compare the outcomes of this work with the findings from previous research, to inform future breakthroughs in electrocatalysis for ethanol oxidation in fuel cells. This study provides us with an opportunity to observe the interaction between WS₂ and OLCs.

2. Purpose of the study

2.1 Aim of the study

The study aims to synthesize Pt/WS₂/N-OLCs composite and develop Pt-based electrocatalysts for the electro-oxidation of ethanol in direct alcohol fuel cells.

2.2 Objectives

- ❖ To synthesize pristine OLCs (p-OLCs) from the waste engine using the flame pyrolysis method.
- ❖ To functionalize and purify p-OLCs using HNO₃ to give functionalized-OLCs (F-OLCs).
- ❖ To dope the F-OLCs with nitrogen using melamine to give nitrogen doped-OLCs (N-OLCs).
- ❖ To synthesize Pt-based catalysts supported on the N-OLCs; and for comparison p-OLCs and F-OLCs.

- ❖ To synthesize WS₂ using the colloidal synthesis method.
- ❖ To synthesize Pt/WS₂/N-OLCs.
- ❖ To test the viability of the synthesized Pt-electrocatalyst for the electrooxidation of ethanol in alkaline media for fuel cells.
- ❖ To characterize the synthesized materials using FTIR, XRD, Raman, TEM, SEM, EDS, and BET.
- ❖ To study the electrochemical behaviour of the synthesized Pt electrocatalyst towards ethanol oxidation reaction in alkaline media.

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Chapter 2: Literature Review

2.1 Carbon materials

The world's fossil fuels are reducing, while on the other hand there is an increasing global demand for energy and the supply is diminishing [1]. It is important to develop new sustainable energy solutions to supplement the existing technologies and mitigate the issue of renewable energy. One way to achieve this, is through the development of innovative new materials that are well performing and sustainable while protecting the environment. Carbon materials are a powerhouse for applications in energy storage and conversion due to their abundance, increased surface area, affordability, eco-friendliness, and its different allotropes and variety of bonding states [2]. Carbon has two main types of polymorphs which are found in nature, and they are (i) graphite, and (ii) diamond [3]. Another addition was discovered in 1985 which was called buckminsterfullerene's/fullerenes by Kroto *et al.*, [4]. Over the years a variety of synthetic allotropes have emerged, and they include carbon nanotubes [5], carbon nanobuds [6], onion-like carbons [7], carbon quantum dots [8], carbon spheres [9], carbon nanofibers [10], carbon nanorods [11], and carbon nanowires [12]. In this study, the advantages of onion-like carbons synthesized from waste engine oil were explored as a support for the Pt-based electrocatalysts for possible application in fuel cells. It is worth mentioning that in some parts of the literature, the onion-like carbons are referred to as carbon nano-onions.

2.1.1 Onion-like carbon

Onion-like carbon (OLCs) belong to the multi-fullerene group, consisting of quasi-spherical and lattice-shaped nano-graphitic sheets of carbon atoms [13]. They were uncovered by Sumio Iijima in 1980 and discussed by Daniel Ugarte in 1992 [14]. Typically, OLCs have a diameter ranging from 1.4 to 50 nm, with a C₆₀ or C₈₀ fullerene at their core and an interlayer distance of approximately 3.4 Å [15]. The specific morphology of OLCs is contingent on the method of preparation, with various techniques available including chemical vapor deposition (CVD), ion implantation, counterflow diffusion flames, annealing of nano-diamonds, electron-beam irradiation, arc discharge, and flame pyrolysis (FP) [13], [16], [17]. Among these methods, flame pyrolysis stands out as a preferred choice due to its energy efficiency, lack of catalyst requirements, and cost-effectiveness [18]. This synthesis technique, utilizing readily available hydrocarbon sources, offers a single-step process that yields higher quantities of OLCs [17].

The unique properties of OLCs, such as a high surface area to volume ratios, low densities, graphitic multilayer structures, biocompatibility, low toxicity, thermal stability, and enhanced conductivity, have garnered significant interest [19]. These properties position OLCs as promising candidates for various applications including catalysis, energy storage and conversion, water treatment, and biomedical uses [20].

2.1.2 Different types of synthesis methods for OLCs

a. Flame pyrolysis method

In this study, the flame pyrolysis (FP) method was used to synthesize OLCs from waste engine oil. The flame pyrolysis method is also identified as the open flame-assisted technique which is an alternate synthesis method for producing catalyst-free OLCs at room temperature [21], [22]. The method was preferred because it does not require complicated equipment, it is affordable, and the carbon sources are simple to obtain and readily available [23]. A variety of carbon sources have been used for the flame pyrolysis method and these include pure oils such as grapeseed oil [23], olive oil [24], ghee oil, cooking oil, coconut oil [25] and flaxseed oil [26]. Waste or used oil such as waste cooking oil has now attracted much attention as the carbon source for the synthesis of OLCs [27]. This is because waste oil was reported to yield OLCs with similar properties, and in some instances enhanced properties as compared to those produced using pure oils. For example, Ntuli *et al.*, reported that the waste vegetable oil-derived OLCs contained C-O-type moieties, and they attributed to the oxygenation process that is said to take place during the frying process [27]. In another study by Das and co-workers, carbon nano-onions (as referred to by the authors) derived from waste frying oil were successfully used as cathode material for zinc-ion hybrid supercapacitors and demonstrated that this material offered excellent long-term durability [28]. These studies show that the FP of waste oil offers cheap alternative way to produce OLCs with excellent properties, hence this study, seeks to explore the use of waste engine oil as a source of carbon to produce OLCs. Figure 2.1 shows a schematic diagram for the FP method where a metal pot is filled with the preferred oil and a wick is placed at the centre of the metal pot [23]. The wick is lit, and a flame is ignited resulting in the burning of oil and the soot is collected on the brass plate placed in the burning flame [26].

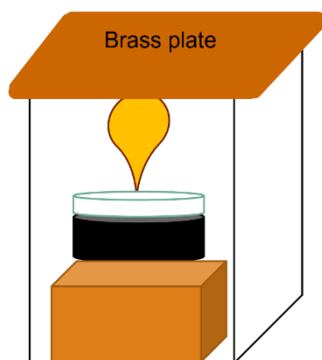


Figure 2.1: Schematic diagram of a flame pyrolysis set up.

b. Chemical vapour deposition

OLCs can also be synthesized through a chemical vapor deposition (CVD) technique where an iron catalyst support is used and supported on sodium chloride to breakdown acetylene gas at about 400 °C [29]. This method results in an increased diameter OLCs in comparison to various preparation methods [30]. He *et al.*, synthesized OLCs from the CVD method using methane with a diameter ranging from 5 to 30 nm [31]. It was reported that this method produced carbon-encapsulated particles and overtime hollow OLCs formed [31]. The CVD method produces high-quality OLCs at a larger scale making it a promising technique [32]. Ali *et al.*, reported the synthesis of OLCs using the CVD method on a NiCo alloy-silica composite prepared through an innovative alcogel electrolysis technique [33]. However, they observed that the OLCs did not perform well for OER due to their increased size coupled with less surface area [33]. An increase in the size of OLCs results in a reduction in their reactivity [34]. Generally, the reactivity of OLCs is dependent on their size and strain [34]. Figure 2.2 shows the schematic diagram of the CVD reactor for the synthesis of OLCs. The process includes using the catalyst ferric nitrate and a material called phenol-formaldehyde resins [30]. It happens at high temperatures, around 1000 °C, causing nanodiamonds to evaporate and then carbon to condense into OLCs on a silicon substrate [30].

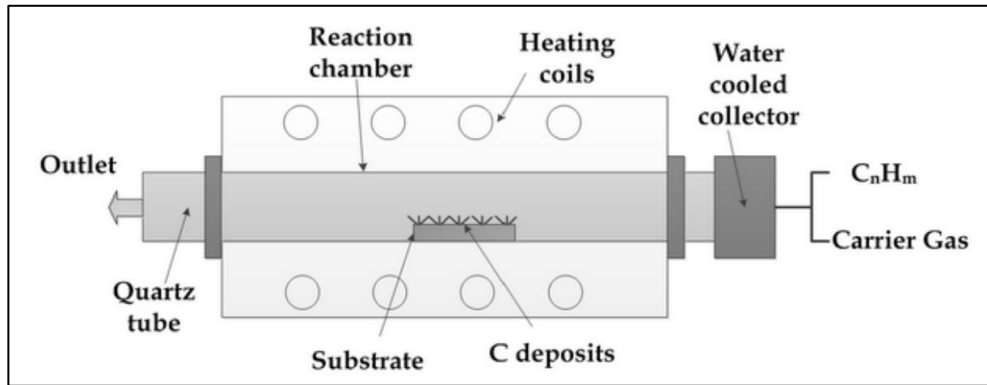


Figure 2.2: Schematic diagram displaying a CVD set up adapted from Gore *et al.*, [30].

c. Ion implantation

The ion implantation procedure involves implanting carbon ions at increased temperatures into a copper or silver base, which is a novel method for forming nearly circular, onion-like carbon structures [35]. Modifying experimental parameters like temperature and the fluence of the implantation can alter the size of the OLCs [35]. This technique was reported by Cabioc'h *et al.*, where increased energy acceleration and mass selection were used to synthesize OLCs in a film state [36], [37]. Thune *et al.*, synthesized OLCs using $^{12}C^+$ and $^{13}C^+$ carbon ion implantations with a range of fluences from 10^{16} to 3×10^{17} ions cm^{-2} conducted into silver substrates while varying the temperature from 400 to 800 °C [38]. The experiment is performed in an implantation chamber [38].

d. Counter flow diffusion flames

It has been shown that OLCs can be synthesized using a variety of methods, but these methods pose an issue because they require high amounts of energy, and the yield is reduced [39]. Extensive scale applications need an easier, uninterrupted, and adequate energy method to synthesize OLCs [40]. Chung *et al.*, examined the influence of acoustic excitation on the production of OLCs using jet diffusion flames and a Ni substrate [41]. It was reported that increased- density OLCs could be synthesized at frequencies closer to the resonant frequencies [41]. Flame synthesis is a suitable technique and is a promising technique for the replacement of the CVD method, however it is challenging to control multiple parameters to obtain quality OLCs [42]. This method requires carbon precursors such as methane, ethylene and even a

mixture of fuels to synthesize OLCs and CNTs using the counter flow diffusion flames. The flame pyrolysis method is cheaper and easily accessible compared to this method hence in this study the FP method was used instead of the counter-flow diffusion flames. The flame pyrolysis method and flame synthesis method are economical and use low energy compared to other methods.

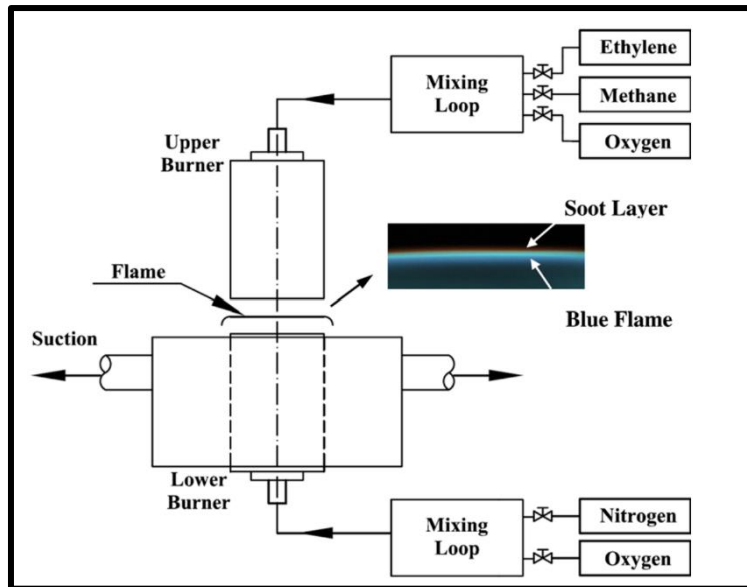


Figure 2.3: A graphical representation of counter flow diffusion flame [38].

e. Annealing of nano-diamonds

Kuznetov *et al.*, were the first to discover a straightforward way to form homogenous and small carbon nano onions of 5 – 8 carbon shells by vacuum annealing at elevated temperatures of ultra dispersed nanodiamonds [43]. Detonation nanodiamonds have been used to aid as a carbon source to produce OLCs in an inactive surrounding by high temperature annealing [44]. This method produces almost perfect onion structures compared to those synthesized using the flame pyrolysis method. Figure 2.4 (a) shows the HR TEM images of OLCs from the annealing of nanodiamonds which shows clear onion rings with a visible interplanar spacing compared to Figure 2.4 (b) which displays OLCs from the flame pyrolysis method where onion rings are not as distinct as the former.

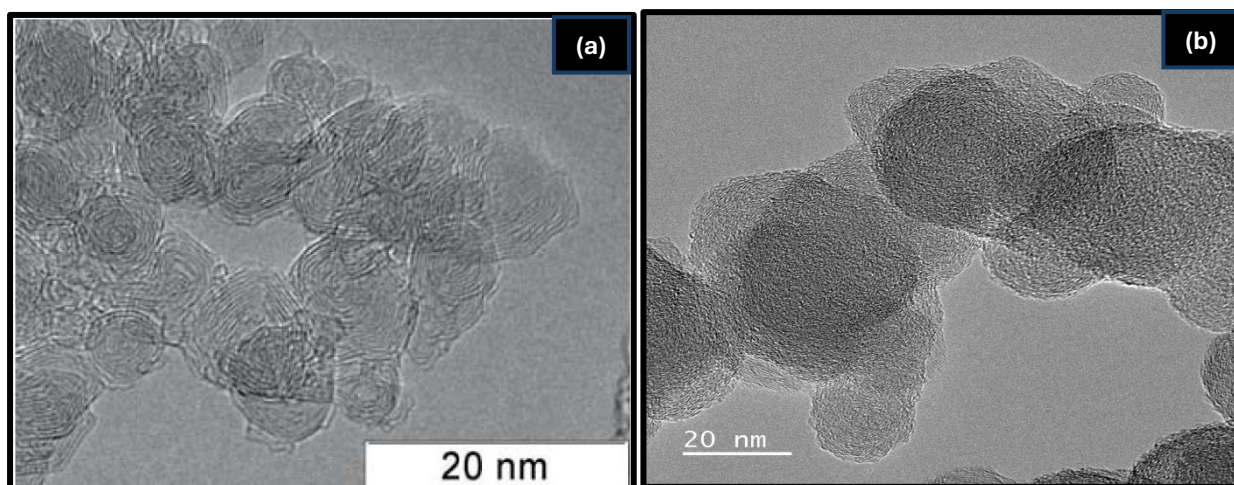


Figure 2.4: HRTEM images of OLCs acquired by (a) annealing of nanodiamonds under vacuum at 1800 K [44] and (b) flame pyrolysis method using waste engine oil [This study].

f. Electron-beam irradiation

Electron beam irradiation converts carbon nanotubes into onion like carbon. Electron beam irradiation is driven by synthesis methods that utilize the electron beam of electron microscopes especially the transmission electron microscope [45]. Li *et al.*, reported the behaviour of MWCNTs when irradiated with an electron beam in FE-TEM [46]. Under electron radiation a morphological change and damage to the MWCNTs was observed whereby the MWCNTs transformed into OLCs [46]. Oku *et al.*, investigated the stimulation of electron beam which prompted the growth of OLCs in the presence of metals that catalyze the formation process [45]. Some of the metallic material may become trapped within the graphitic layers, resulting in hybrid structures with metallic atoms intercalated between the graphitic layers [47]. Overall, the metals' catalytic function is to hasten the process by aiding in the rupture of C–C bonds through the direct transfer of some of the absorbed energy from the main beam [47]. This method is perfect for an in situ type of synthesis because you watch the transformation happen in real time [48].

g. Arc discharge

Sano *et al.*, noted a countertop technique for an increased scale synthesis of OLCs by hitting an arc at 16 – 17 V, 30 A between 2 pure graphite electrodes immersed under deionized water [49]. The arc discharge method offers the benefit of combining a decent production rate with a very straightforward experimental setup [50]. The commonly employed techniques for creating carbon nanomaterials involve vacuum setups for plasma generation via an arc discharge, laser ablation, or glow discharge [51]. Additionally, vacuum processes result in undesired contaminants like amorphous carbon and disordered nanoparticles, necessitating time-consuming and costly purification steps [51].

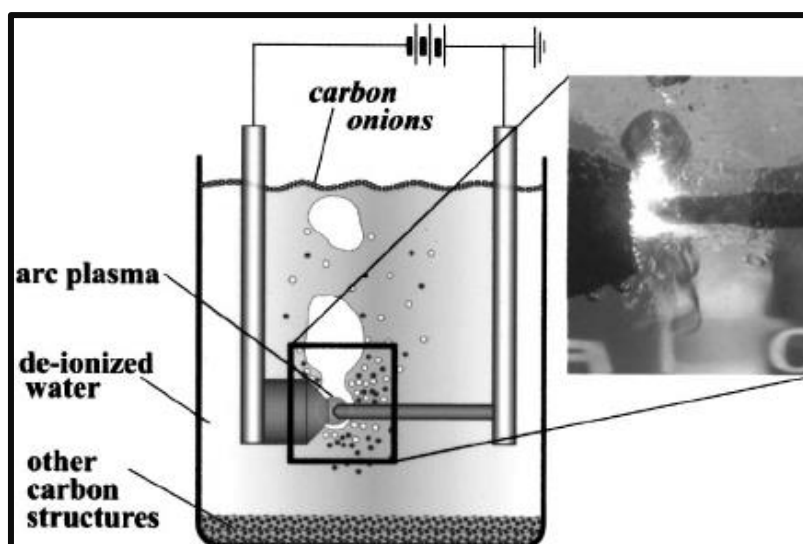


Figure 2.5: Simple experimental set up for arch discharge adapted from Sano *et al.*, [50].

2.1.3 Applications of OLCs

a. Supercapacitors

Electric double-layer capacitors (EDLC), also called supercapacitors or ultracapacitors in the market, are devices used for storing electrical energy without undergoing chemical reactions [29]. They accumulate charge on a carbon electrode with an increased surface area, typically made from porous activated carbon [29]. Supercapacitors have been explored as a substitute

for traditional batteries for electronic vehicles [52]. The main issue with supercapacitors is that they have decreased energy densities regardless of their higher power densities [23]. Carbon-based materials, such as activated carbons (ACs), carbon nanotubes (CNTs), and carbon-based composites, have been employed as active electrodes for energy storage because they are inexpensive, exhibit good stability, and are readily accessible [53]. The dual properties of increased electrical conductivity and simple ion availability through the outer surface area result in OLCs being very appealing for high - power applications that need quick charge and discharge rates [54]. It was observed in the literature that OLCs offered attractive properties for EDLCs and have shown a higher specific capacitance than MWCNTs [55]. Sun *et al.*, prepared OLC/graphene and used them as electrodes for supercapacitors without any modifications [56]. The OLCs in the OLC/graphene composite eliminated the agglomeration of the hydrophobic graphene sheets during the reduction of graphene oxide thus increasing the specific surface area and improving the performance of the supercapacitor [55], [56].

b. Batteries

Lithium-ion batteries (LIBs) are one of the most used batteries in the world for portable electronic devices, power tools, and vehicles powered by electricity due to their attractive properties of high energy and power density [57]. The material that makes up the anode is a very crucial aspect in the innovation and marketing of the lithium-ion battery [58]. The anode should exhibit properties like capacity, rate efficiency, and cycling stability which contribute to the efficiency of the lithium-ion battery [59]. It has been reported that the issue that arises with present anode candidates with increased capacity such as FeS is reduced electrical conductivity [60]. Another limitation of the anode materials is the agglomeration experienced during the cycling process which can negatively impact the capacity fading and rate performance [61]. As already mentioned, OLCs have excellent conductivity and stability properties and have been used to mitigate the limitations found within the anode materials for LIBs and Na ion batteries [61], [62]. The combination of Mo₂C nanoparticles enclosed in onion-like carbon (OLC) and surrounded by amorphous carbon (a-C) has been demonstrated to reduce the clustering effect. The Mo₂C@OLC/a-C nanocomposites showed an initial Coulombic efficiency of 75.1% and maintained a capacity of 708 mAh.g⁻¹ at 0.1 A. g⁻¹ and 480 mAh.g⁻¹ at 2 A.g⁻¹ after undergoing 100 cycles [63]. Wang *et al.*, showed that MoS₂/OLC nanocomposites exhibit improved electrochemical performance in comparison to regular MoS₂ powder when used as anode materials in lithium-ion batteries (LIBs) [64]. They achieved a

specific capacity of 853 mAh.g⁻¹ at a current density of 50 mA g⁻¹ after 60 cycles, along with a moderate initial coulombic efficiency of 71.1%. This indicated the potential of OLCs for enhancing the efficiency and performance of LIBs [64].

c. Dye sensitized solar cells (DSSCs)

Carbon nanomaterials have been explored for the application of DSSCs [65]. A conventional DSSC typically employs a conductive counter electrode made from either fluorine-doped tin oxide (FTO) or glass with a titanium dioxide (TiO₂)-based electrolyte [66]. The process of scaling up the industrial fabrication of DSSCs presents a challenge because of the expensive and scarce platinum used in the counter electrode. Therefore, using a more affordable replacement material is ideal [67]. Due to its increased surface area, electrical conductivity, and chemical stability OLCs have proven to perform well as counter electrodes [68]. Mohapatra *et al.*, showed that carbon nano onion (CNO) counter electrodes are promising due to their optical transparency, satisfactory electrochemical redox activity for the I⁻/I₃⁻ redox couple, and exchange current density like Pt counter electrodes [69]. DSSCs powered by CNO exhibited optical transparency exceeding 55% and achieved a notable solar energy conversion efficiency of 5.17% [69]. Pang *et al.*, assembled DSSC using the N-CNOs/mGr electrode which exhibited superior long-term stability and a higher power conversion efficiency of 10.28% compared to devices utilizing conventional Pt (6.54%) and mGr (5.11%) electrodes [70].

d. Water treatment

Dyes are the prominent substances released by industries in effluents that pollute surface water which is unsafe for aquatic life and humanity and can affect health [71]. For instance, methylene blue, which is widely used in the textile industry, and tannins, when discarded improperly into effluents, could be detrimental to the environment, resulting in the bioaccumulation of the dye [72]. Therefore, it is imperative to innovate technologies aimed at purifying water and wastewater tainted with such persistent pollutants. Electro-Fenton, Fenton and Fenton photo-assisted procedures are the most used, but these processes are expensive [73]. Ntuli *et al.*, took advantage of the properties of OLCs synthesized using waste cooking oil to evaluate their effectiveness in removing hexavalent chromium ions from water [27]. Kumari *et al.*, used CNOs synthesized from flaxseed oil as an effective adsorbent for the removal of poisonous oxo-anions [74].

2.2 Two-dimensional transition metal dichalcogenides (TMDs)

Numerous 2D structures exist in abundance, comprising stacks of strongly bonded layers with weak interlayer attraction, facilitating the flaking process into individual atomic thin layers [75]. Transition metal dichalcogenides have become the foundation of research and technological applications because of their distinct crystal structures due to their wide range of chemical compositions [76]. Graphene was considered a great 2D material but the problem with graphene was that it has no sizeable energy gap which can be limiting especially in catalysis [77]. TMDs exhibit a universal structure of MX_2 , where M is the transition metal group IV, V, or VI on the periodic table, and X signifies a chalcogen (S, Se, and Te) [77]. These materials are known to exhibit opulent electronic, mechanical, optical, and chemical characteristics [78]. There are a variety of TMD metals, and these include MoS_2 , WS_2 , MoSe_2 , WSe_2 , and MoTe_2 . In this study WS_2 particularly be used as a co-catalyst to the Pt composite with OLCs being the support [79]. An intriguing aspect of Transition Metal Dichalcogenides (TMDs) is that they are semiconducting structures and have different polymorphs which include 1T phase, 1H phase, 2H phase, and 3R phase known as rhombohedral phase (Figure 2.6) [80].

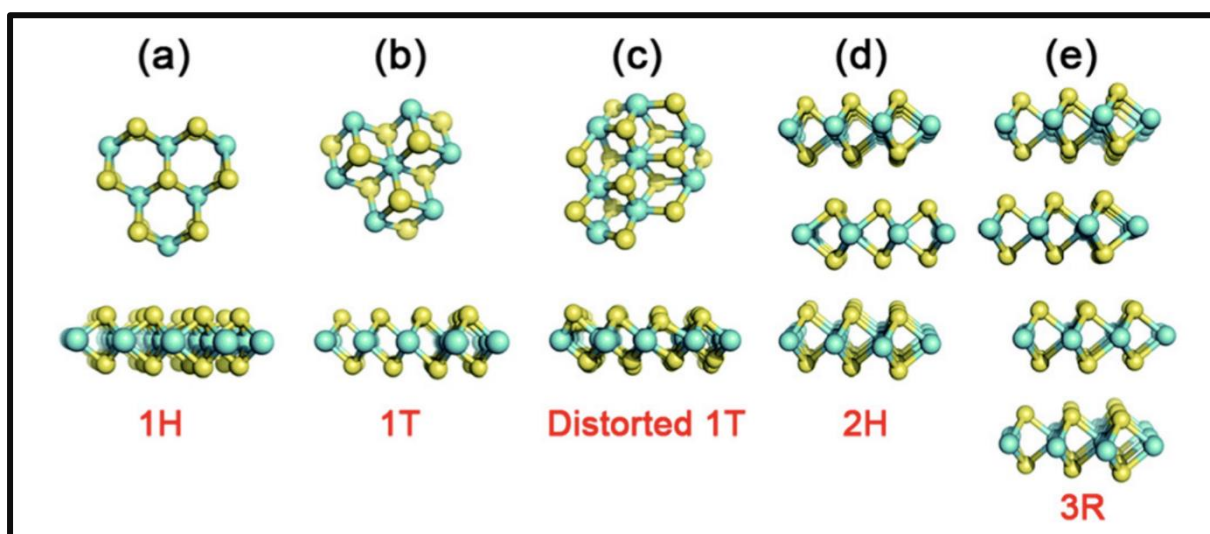


Figure 2.6: Polymorphs for Transition Metal Dichalcogenides (TMDs) adapted from [56].

2.2.1 Tungsten disulfide (WS₂)

Transition metal dichalcogenides (TMDs) like MoS₂, WS₂, WSe₂, and MoSe₂ are ultra-thin 2D materials exhibiting remarkable electronic, magnetic, and optical properties, along with a layered structure [81]. WS₂, being a 2D material with a substantial specific area and thus abundant active sites, is expected to excel in catalytic performance due to its superior electrical conductivity, and numerous catalytic active sites for hydrogen evolution, as highlighted in recent research [82]. Among these, WS₂ stands out as an active catalyst for the Hydrogen Evolution Reaction (HER) due to its cost-effectiveness, strong chemical cohesion, and abundant availability [83]. Enhancing WS₂ with metal doping, such as platinum, boosts its performance, although its intrinsic electronic structure can limit electronic conductivity [83]. The sandwich-like S-M-S structure of WS₂, with sulphur atoms encapsulating metal atoms, leads to robust redox catalysis, particularly suited for Oxygen Reduction Reaction (ORR) in alkaline environments [84]. Research by Vautttiki *et al.*, indicates that rGO@WS₂ exhibits improved stability and performance in methanol oxidation and oxygen reduction in alkaline conditions [85]. Strategically chosen catalyst supports can prevent WS₂ nanostructures from clustering, thereby enhancing overall functionality [86]. Synthesizing WS₂ nanoflowers via hydrothermal and CVD routes allows for precise control over morphology, contributing to superior WS₂ properties [87]. The exceptional properties of WS₂ have spurred interest across diverse applications, including energy storage, supercapacitors, solar cells, biosensors, and lithium/sodium-ion batteries [85]. In this study, the properties of WS₂ were leveraged to enhance the performance of the Pt-based composite. While most literature studies concentrate on reactions such as HER, ORR and OER, limited research has been conducted on the oxidation of ethanol.

2.2.2 Applications of WS₂

a. Catalysis

WS₂ has a variety of applications in the field of catalysis and has been used as an electrocatalyst and a photocatalyst due to its distinct bandgap, void imperfections, and reduced conductivity [88].

Photocatalysis

The crystal structure, surface area, and morphology of a material play an important role in the performance of the material as a photocatalyst [89]. The higher the surface area the more active sites are available for the promotion of charge migration of photo-generated electron-hole pairs [90]. WS₂ has attracted much attention due to its unique bandgap which undergoes an indirect (1.4 eV) to direct (2 eV) when the size is decreased from bulk to single layer and its semiconducting abilities [91]. WS₂ exhibits excellent photocatalytic properties due to its vast spectrum absorption of visible light. It has demonstrated enhanced performance in photocatalytic reactions, including the degradation of dyes like rhodamine B, generation of H₂, and reduction of nitrophenol [89]. A drawback observed during photocatalytic reactions is that accelerated recombination of excitons occurs therefore pure WS₂ is weak and prevents surface charge migration [92]. To combat this issue the use of composites has proven to improve photocatalysis using WS₂ [93]. Nawaz *et al.*, prepared g-C₃N₄/WS₂ achieved via one-step hydrothermal synthesis without using a reducing agent for the development of a p-n heterojunction photocatalyst which demonstrated improved performance for solar energy in a durable photocatalysis reaction [94]. Zhong *et al.*, suggested a new method to improve the effectiveness and durability of photocatalysts by tackling the problem of photo corrosion in CdS through its interaction with WS₂ nanosheets, leading to a durable and effective CdS/WS₂ photocatalyst that shows better rates of H₂ production and long-lasting stability [95].

Electrocatalysis

WS₂ is a structure that has layers with adjustable electronic features and exposed edges as active sites [96]. WS₂ has been mostly used as an electrocatalyst for hydrogen evolution reactions. The exterior of WS₂ is inactive, and the electrocatalytic activity occurs at the outer border of WS₂ which dictates the overall catalytic performance and conductivity [97]. WS₂, being a semiconductor, exhibits limited electrical conductivity and a reduced ability to transfer electrons, thereby constraining its electrocatalytic activity to some degree [97]. For WS₂ to exhibit a distinctive catalytic effect, it requires complete contact with the electrolyte across its layer. Two innovative strategies have been proposed: (a) enlarging the active surface areas by exposing the edges to the electrolyte [98], and (b) boosting the inherent activity of individual active sites [98]. To improve the performance of WS₂ in electrocatalysis doping of WS₂ has been explored using oxygen and nitrogen. Composites using WS₂ as a co-catalyst have been proven to enhance the performance of the material in electrocatalytic reactions [99]. Jing *et*

al., crafted a WS₂/CoS₂ heterostructure on carbon paper (CP) using a three-step process. The WS₂/CoS₂ heterostructure showed remarkable electrocatalytic activity due to a synergistic effect, displaying a low overpotential of 245 mV at 100 mA/cm² and a small Tafel slope of 270 mV/dec for the hydrogen evolution reaction (HER) [100]. Not many studies have been done for the electrooxidation of alcohol using pure WS₂ which shows that WS₂ excels when coupled with another material. Xu *et al.*, supported WO₃ – WS₂ on mesoporous N, S co-doped carbon using a single-step molten-salt method, resulting in an improved interaction between metal and carbon. This enhanced interaction led to increased selectivity in oxidizing benzyl alcohol to benzaldehyde.

b. Lubricants

Micro- and nano-sized WS₂ particles demonstrate exceptional anti-friction properties, offering effective solutions to dynamic friction challenges encountered in the mechanical production processes involving WS₂ [89]. An interesting aspect of WS₂ is that the layers interact by weak van der Waals forces which allows for interlayer gliding thus reducing the friction coefficient [101]. Yan *et al.*, fabricated distinct WS₂ films with varying structures and integrated them with space lubricating oils to create unique WS₂/oils composite lubricating systems [102]. The friction and wear properties of these systems were primarily investigated under vacuum conditions. The findings revealed that WS₂/P201 systems exhibit significantly lower friction coefficients ($\mu \approx 0.06$) compared to WS₂/PFPE systems ($\mu \approx 0.11$), with this difference attributed to the lubricating properties of the oils [102].

c. Gas sensing

Consistent and dependable monitoring of diverse gases plays a critical role in industrial process surveillance, controlling vehicle emissions, ensuring indoor and outdoor air quality, and safeguarding environmental well-being [103]. Sensors have arrays that are highly effective in distinguishing and quantifying analytes reliably, their functionality is limited to high-temperature conditions, which in turn demands significant power resources for operation [104]. WS₂ is progressively gaining ground in comparison to its TMDC counterpart, MoS₂, in terms of research efforts focused on its ability to detect NH₃ gas [87]. Gqoba *et al.*, employed a one-step colloidal method to fabricate WS₂ nanoflowers, which were then utilized as a chemical sensor for detecting ammonia gases at ambient temperature. The WS₂ nanoflowers exhibited enhanced selectivity and reactivity towards ammonia [87], [105].

2.3 Platinum – based electrocatalysts for direct ethanol fuel cells

Platinum is known to be very stable and exhibits increased stability thus making it an appropriate electrocatalyst for the electrooxidation of a variety of compact chemical molecules [106]. At room temperature pure platinum catalyst does not perform well for ethanol and methanol electrooxidation due to the poisoning of the adsorbed intermediates [107]. At a reduced functioning temperature, the prevalent poisoning compound is CO [106]. Various metals, including gold, rhodium, and palladium, have been studied as potential catalysts for ethanol electro-oxidation, alongside platinum [108]. While these metals exhibit certain levels of activity, previous research indicates that platinum stands out as the most effective catalyst for practical applications, especially in acidic environments where it remains the only active and durable noble metal catalyst [109]. The properties and structure of the electrode material play a crucial role in how ethanol is adsorbed and electro-oxidized, influencing the formation of intermediate products [110]. To expedite progress in developing direct ethanol fuel cells (DEFCs), there's a need to create highly efficient anode catalysts specifically tailored for ethanol oxidation [111]. Research has focused on improving the performance of Pt based electrocatalysts for the application of DEFCs [112].

2.4 Direct alcohol fuel cells (DAFCs)

Sir William Grove is credited with inventing the fuel cell in 1839, which is an electrochemical device converting the heat from fuel combustion (such as hydrogen, natural gas, methanol, ethanol, and hydrocarbons) into electricity [113]. Direct alcohol fuel cells (DAFCs) are particularly notable for their application in lightweight electronic devices, increased power production, and automotive use. The demand for improved power sources has grown significantly over time [114]. Currently, DAFCs primarily use acidic proton exchange membranes. The presence of a strong acidic electrolyte membrane facilitates the easy discharge of CO₂ formed during the anodic reaction [115]. However, DAFCs face challenges such as poor performance due to kinetic limitations in alcohol oxidation reactions in acidic environments, which can be addressed by using basic media [115]. Alcohols like methanol, ethanol, ethylene glycol, and glycerol offer higher volumetric energy density and easier transportation and storage compared to hydrogen [116]. Despite their advantages, DAFCs have limitations, including Pt-based catalysts that are sensitive to CO poisoning, alcohol crossover,

partition deterioration, and degradation of carbon nanomaterials and cell hardware [116]. The operating principles of DAFCs can be illustrated using a direct ethanol fuel cell (DEFC) as an example. Figure 2.7 shows a simple schematic diagram that shows what a typical direct ethanol fuel cell would look like. The electrochemical cell comprises three main components: a proton exchange membrane for ionic conduction, a cathode, and an anode serving as electrodes [113]. Anhydrous or diluted ethanol in liquid or gaseous form is directly supplied to the anode cell, while air is supplied to the cathode cell. At the electrode-electrolyte interface, ethanol undergoes oxidation to generate protons, carbon dioxide, electrons, and partially oxidized ethanol intermediates/products like acetaldehyde and acetic acid [117]. The electro-oxidation reaction of ethanol at the anode is represented as follows:



The electro-reduction reaction of ethanol at the cathode is represented as follows:



Overall cell reaction:

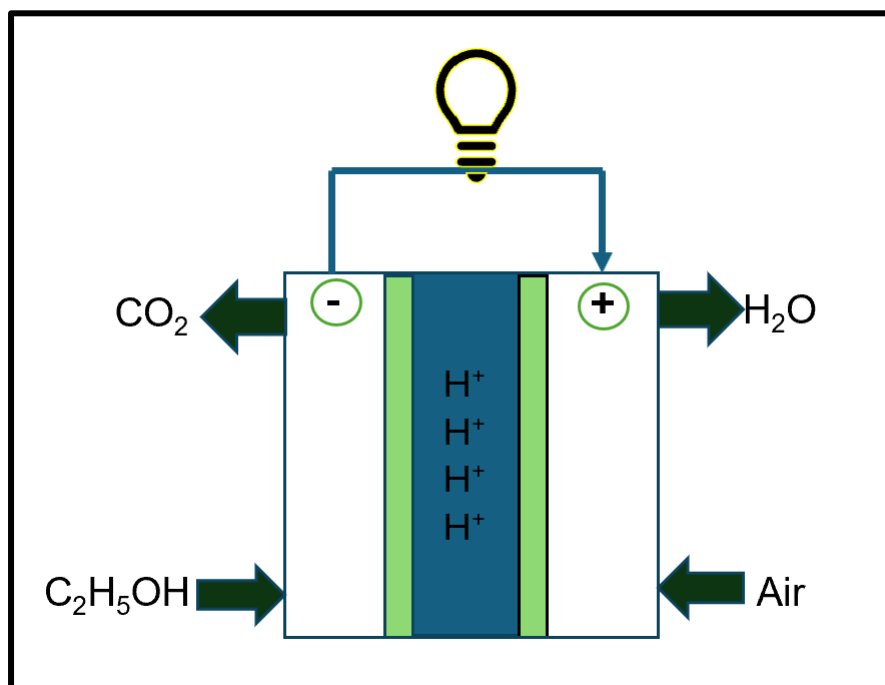
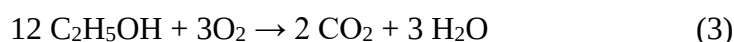


Figure 2.7: A simple graphical representation of a direct ethanol fuel cell.

2.5 OLCs and the corresponding composites as catalyst supports in DAFCs.

Researchers continually discover innovative methods to incorporate electrocatalysts, enhancing the performance of direct alcohol fuel cells. Various studies have been conducted where OLCs were used as a support for composites used in the application of DAFCs. Lou., et al synthesized OLCNs (onion-like nanocarbons) as referred to by the authors using affordable and accessible candles as a carbon source [118]. For the composite, an effortless one-pot surfactant-free solvothermal synthesis was employed to form PtSn/OLCNs. The PtSn/OLNCs nanocomposites achieved outstanding electrocatalytic performance with a Pt content of approximately 10.1 wt.%, showcasing remarkable activity for methanol oxidation reactions (MOR) and ethylene glycol oxidation reactions (EGOR) [118]. Compared to the commercial 20 wt.% Pt/C catalyst, the PtSn/OLNCs exhibited current densities 2.6 and 2.7 times higher for MOR and EGOR, respectively, highlighting their promising prospects for utilization in direct alcohol fuel cells (DAFCs) [118]. Sikeyi *et al.*, fabricated Pd/p-CNO, Pd/ox-CNO, and Pt/N-CNO, and it was reported that both the N-CNO and Pd/N-CNO electrocatalysts demonstrated elevated current density (4.2 mA.cm^{-2} and 17.4 mA.cm^{-2}), sustained stability over time (1.2 mA.cm^{-2} and 6.9 mA.cm^{-2}), and rapid electron transfer in contrast to their respective pristine and oxidized counterparts (including Pd variants), as well as a commercial Pd/C electrocatalyst. These findings were observed during ethanol oxidation reactions in an alkaline environment [17].

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Chapter 3: Characterization techniques

3.1 Introduction

In material science, it is important to understand the functional, chemical, structural properties and surface chemistry of the nanomaterials synthesized in the laboratory. This information helps us understand the behaviour and chemistry of nanomaterials. In this chapter, we will explore the characterization techniques used in this study to characterize the synthesized electrocatalysts.

Electrocatalysts have significant variables, which include texture and chemical surface relating catalytic activity to their properties [1]. In this study, a variety of techniques was employed to investigate the morphological, chemical, and structural properties of the synthesized electrocatalysts. These characterization techniques include Fourier transform microscopy, powder X-ray diffraction, Raman spectroscopy, transmission electron microscopy, Brunauer-Emmett-Teller analysis, scanning electron microscopy, energy dispersive X-ray spectroscopy, thermogravimetric analysis, and X-ray photon spectroscopy.

3.2 Analysis techniques used for the synthesized electrocatalysts

3.2.1 Fourier transform microscopy

Fourier transform infrared (FTIR) spectroscopy has a rich historical background of obtaining the fingerprints of chemical compounds along with reaction intermediates [2]. This technique obtains an infrared spectrum in a whole array of wavenumbers concurrently [3]. FTIR is a vibrational spectroscopic characterization technique that is non-invasive, basic, repeatable, requires a reduced amount of sample, and entails effortless sample preparation [4]. The FTIR device transmits infrared radiation ranging from approximately 10,000 to 100 cm^{-1} across a sample, where some of the radiation is absorbed while the rest passes through. Molecules in the sample convert the absorbed radiation into rotational and/or vibrational energy [2], [3], [4], [5], [6]. As a result, the detector records a spectrum usually spanning from 4000 cm^{-1} to 400 cm^{-1} , revealing a distinctive molecular pattern of the sample. Each molecule or chemical structure yields a distinct spectral pattern, rendering FTIR analysis highly effective for identifying chemicals [5]. Over the years waste materials have been a serious problem and understanding how they interact with the environment and how they negatively impact the environment is very important. Techniques such as the FTIR tell us what these waste materials are composed of and with that information we can handle, store, or discard the waste materials safely [6]. In this study, waste engine oil was used to synthesize OLCs as the support material

for the electrocatalysts. Figure 3.1 shows the Bruker Tensor 27 FTIR instrument which was used to analyze the chemical composition of the waste engine oil and determine the functional groups present. This analysis aimed to understand how these functional groups influence the performance of the OLCs.



Figure 3.1: Bruker Tensor 27 FTIR instrument.

3.2.2 Powder X-ray diffraction

Powder X-ray diffraction (PXRD) is a well-known characterization technique in materials science, chemistry, physics, and crystallography. Scientists have determined that crystalline substances function as three-dimensional diffraction gratings for X-ray wavelengths, akin to the spacing between planes in a crystal lattice [7]. PXRD is a characterization technique used to investigate the geometric configuration of the crystal structure of the material, classification, and measurement of crystalline forms [8]. The main advantages of using PXRD include (i) simple data collection, (ii) non-destructive method, (iii) easier sample preparation, and (iv) materials that have unique XRD patterns [9]. PXRD shows the dispersed intensity vs 2θ (Bragg angle) which has several signals known as reflections [10]. Due to the orderly alignment of atoms within solid objects, the coherent scattering of X-rays by these atoms leads to constructive interference occurring at specific, clearly defined angles [10].

The diffraction responds to multiple refracted beams that meet the Bragg's law for constructive interference [11]:

$$n\lambda = 2d\sin\theta \quad \dots \text{Equation 3.1}$$

Where:

n – positive integer

λ – Wavelength

d – Spacing of atomic planes

θ – angle of incidence and reflection

Equation 3.1 is Bragg's law and Figure 3.2 shows a schematic representation of Bragg's law. The crystallinity and interlayer spacing of the synthesized materials were assessed using Powder X-ray Diffraction (XRD) Bruker D2 phaser with monochromatic Cu K α radiation shown in Figure 3.3; characterized by a wavelength of $\lambda = 0.1505$ nm, produced at 30 kV and 10 mA. The diffraction peaks were compared to those of standard nanomaterials from literature references, using the EVA software package within the diffraction plus evaluation package for analysis.

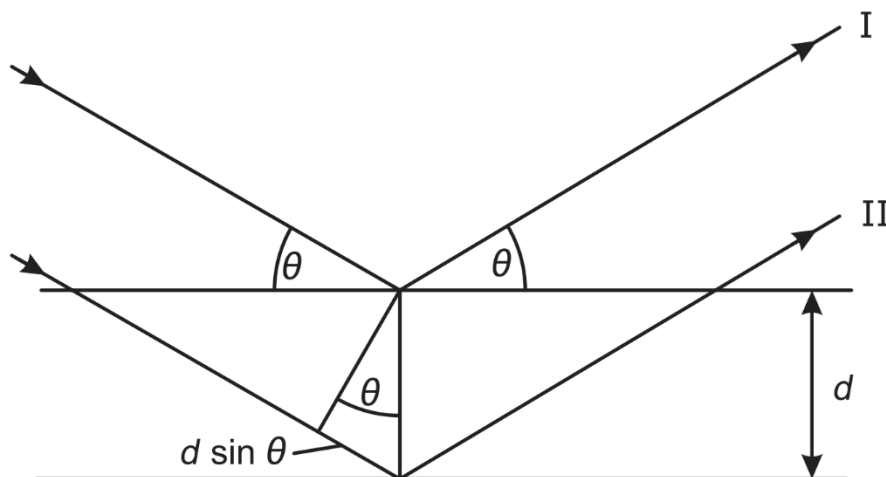


Figure 3.2: Schematic representation of Bragg's law [3], [8], [9], [10], [11].

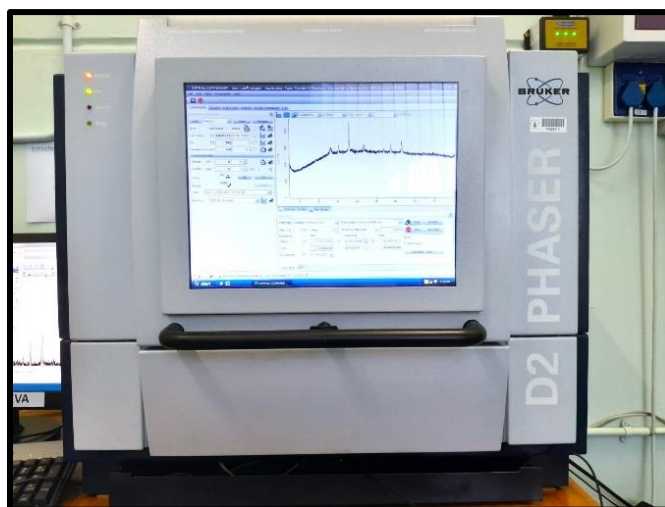


Figure 3.3: Bruker D2 phaser PXRD instrument.

3.2.3 Raman spectrometer

Raman spectroscopy is a technique used for examining and mapping nanomaterials scattered in an array [12]. Two important terms that need to be understood in Raman spectroscopy, Raman effect and Raman scattering. Raman effect is a two-photon process where the photon that is radiated is dependent on the alteration of the polarizability during the phonon movement [13]. Raman scattering is a principle of electromagnetic radiation of molecules. When exposing nanomaterials to electromagnetic radiation of a singular frequency, the light will scatter from molecules in both elastic and inelastic manners [3]. Stokes lines are a consequence of the increase in the frequency of the incident radiation compared to the frequency of the scattered radiation [14]. Alternatively, when the opposite happens, anti-Stokes lines appear. The information that can be deduced from Raman spectroscopy includes structure, symmetry, electronic environment, and chemical bonding of the material; this allows for the quantitative and qualitative evaluation of the individual compounds [15]. The LabRAM HR Raman spectrometer from HORIBA scientific was used to analyse the quality of the nanomaterials synthesized in this study.

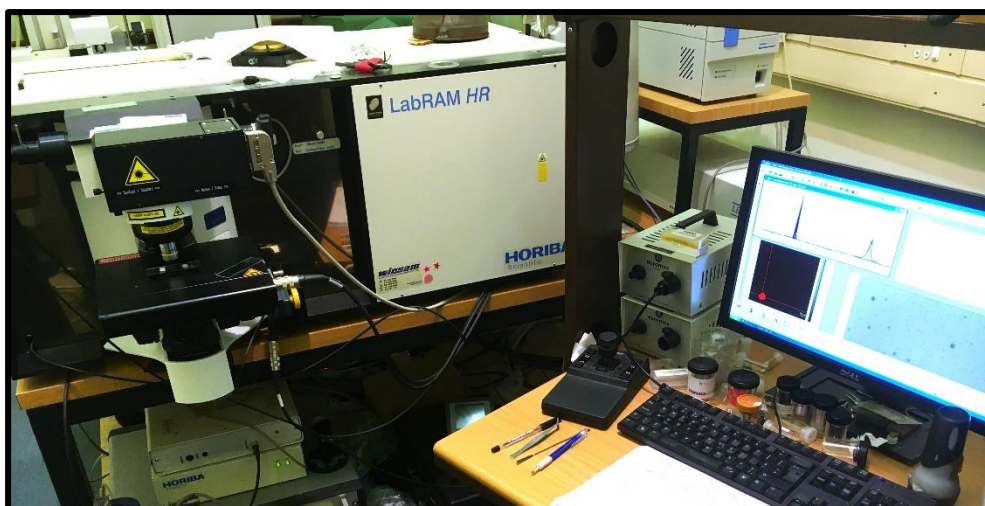


Figure 3.4: LabRAM Horiba Raman spectrometer instrument.

3.4 Transmission electron microscopy

Transmission electron microscopy (TEM) works similar to transmission light microscopy [3]. The only difference is that TEM uses an electron ray and electron beam instead of a visible light ray and electromagnetic lens [3]. TEM is considered a convenient and formidable technology used for imaging nanomaterials [16]. TEM was used to determine the morphology, crystallography, atomic, and electronic structure of the synthesized electrocatalysts [17], [18]. This technique can also be used for chemical composition and bonding. TEM is bombarded with an increased voltage electron beam to generate an image. The electron gun is found at the top which creates the electron that moves in the vacuum tube. The electromagnetic lens is used to fixate the fine beam electrons that move through the ultra-thin specimen. The fluorescent screen is located at the base of the microscope and is hit by the transferred electrons this results in the formation of the image of the different parts of the sample [17], [18]. TEM was used to characterize the synthesized nanomaterials in this study and TEM requires sample preparation because the sample needs to be thin [3], [16]. The nanomaterials were dispersed in ethanol and about 5-10 drops of the solution were dropped on to the copper grid. Figure 3.5 shows the FEI TECNAI SPIRIT TEM instrument used in this study.

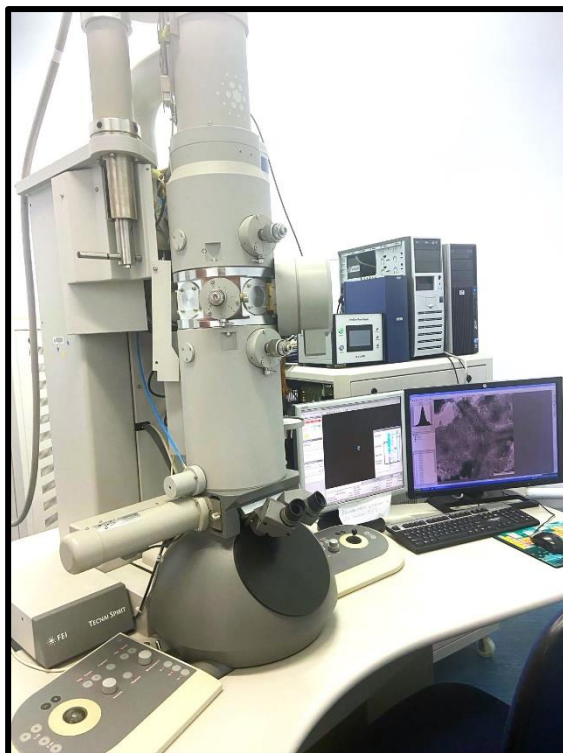


Figure 3.5: FEI TECNAI SPIRIT TEM instrument.

3.2.5 Brunauer-Emmett-Teller analysis

Brunauer-Emmett-Teller (BET) was initially developed to determine the present surface area in a material that employs a probe molecule to move singular molecules which are known as the geometry-based approach and the other approach used is the isotherm-based approach which focuses on generating the monolayer coverage based on the BET theory [19]. Langmuir's theory is explained through a kinetic model of the adsorption process where it is determined that the adsorption is confined to a single monolayer and the dynamic equilibrium is met between the gas phase and the adsorbed state [20]. The rate of adsorption and desorption must be equal [20]. The surface areas of the OLCs synthesized in this study were determined from gas adsorption isotherms at the boiling point of nitrogen gas [21]. Nitrogen gas is the most used gas, however argon, carbon dioxide, and other organic vapours can be used [21]. The micrometrics TriStar II plus BET instrument was used to determine the surface area, and pore size of the synthesized OLCs in this study.



Figure 3.6: Micrometrics TriStar II plus BET instrument.

3.2.6 Scanning electron microscopy and energy dispersive spectroscopy

Scanning electron microscopy (SEM) analysis has been applied in a variety of fields and is seen as an efficient characterization technique for organic and inorganic materials in a nm to a μm range [22]. SEM works at an increased magnification reaching $300\,000\times$ up to $1\,000\,000$ (in the recent models) to generate images (3D) for a variety of materials [22]. SEM is coupled with energy dispersive X-ray spectroscopy (EDS) because they are a synergistic pair to provide qualitative and semi-quantitative information [22]. These techniques work together to gather information about the synthesized materials. SEM provides the images while EDS gives the elemental composition. This was important for this study to characterize the synthesized nanomaterials. The advantages of SEM include (i) easy sample preparation; (ii) allowing for the analysis of increased surface area; and (iii) rotating and tilting specimen holders to observe the different orientations of the sample [23]. Figure 3.7 shows the Zeiss Sigma 03-39 Fe-scanning electron microscope which is coupled with EDS.



Figure 3.7: Zeiss Sigma 03-39 Fe-scanning electron microscope.

3.2.7 Thermogravimetric analysis

Thermogravimetric (TGA) analysis is a method whereby the mass of a sample is measured over a period as the temperature alternates [24]. The nanomaterial is heated in the provided conditions which could be air, N₂, CO₂, He, or Ar at a regulated temperature [24]. The temperature is raised at a fixed cadence where the starting weight of the nanomaterial is known and the weight changes are recorded [24]. TGA is mostly used to determine the thermal properties, and impurities of minerals, polymers, and carbon materials [25]. TGA is a dynamic analytical tool that provides a plethora of information including qualitative and quantitative information that can be corroborated with other characterization techniques [25]. In this study, TGA (Figure 3.8) was used to determine the stability of the synthesised OLCs from waste engine oil. The TGA was used to monitor the thermal degradation profile of the OLCs materials after doping and dispersing Pt on the OLCs support [26].



Figure 3.8: Perkin Elmer 4000 thermogravimetric analyser.

3.2.8 X-ray photon spectroscopy

X-ray photon spectroscopy (XPS) is a technique that is mainly used for surface analysis whereby X-rays are pelted on the surface of the sample and the kinetic energy of the released electrons is measured [27]. XPS uses the concept of the photoelectric effect [28]. What makes XPS unique is the ability to determine the chemical state information from the elements in the material [27]. For this study, the ESCALAB 250Xi XPS instrument (Figure 3.9) was used to determine the elemental composition and electronic/chemical state and confirm the doping of N-OLCs, formation of WS₂ and the Pt-based electrocatalysts [29].



Figure 3.9: ESCALAB 250Xi XPS instrument

3.2.9 Electrochemical characterization

A potentiostat was used to measure the cyclic voltammetry as the electrochemical characterization. A potentiostat is an electrochemical instrument that controls the voltage applied to an electrochemical cell and measures the resulting current [30]. Cyclic voltammetry is a fundamental electrochemical technique for studying the redox properties of chemical systems [30].

A typical setup for CV includes:

- ❖ A working electrode (eg., glassy carbon, platinum),
- ❖ A counter electrode (Often platinum or a similar inert material),
- ❖ A reference electrode (such as a Ag/AgCl or a silver wire pseudoreference electrode).

This three-electrode system is connected to the potentiostat, which applies a variable voltage and records the resulting current, generating a cyclic voltammogram [31]. The shape of the voltammogram and the relationship between the anodic (oxidation) and cathodic (reduction) peaks provide information about whether the electron transfer process is reversible, quasi-reversible, or irreversible [31]. The electrochemical characterization was done on a Biologic SP 300 potentiostat.

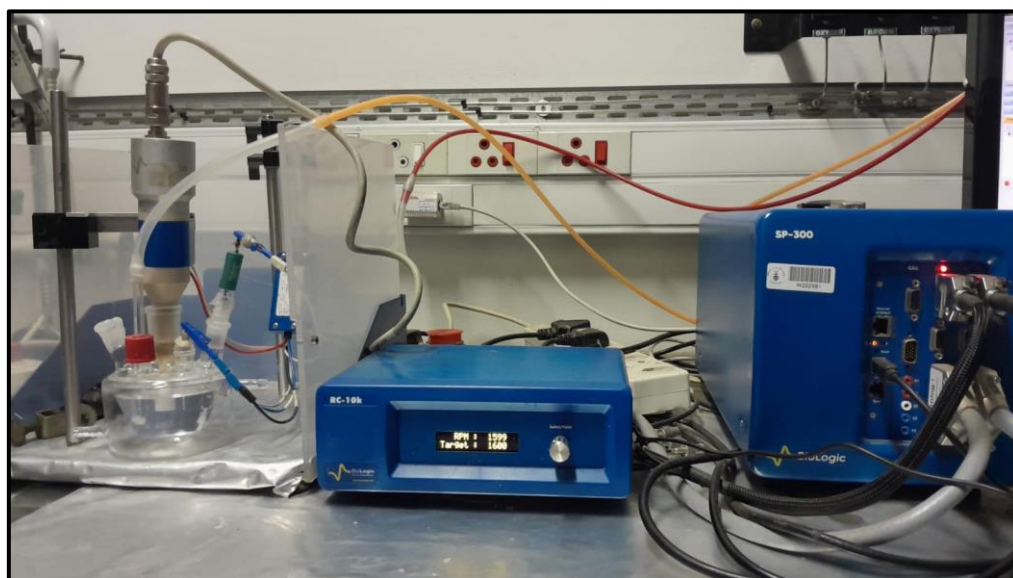


Figure 3.10: Biologic SP 300 potentiostat

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Chapter 4: Synthesis, doping and functionalization of onion-like carbons from waste engine oil

4.1 Introduction

The study of carbon materials has been ongoing, and these materials have been widely used in a variety of applications. Onion-like carbon (OLCs) nanomaterials have been recently introduced to the existing carbon allotropes and are part of the multi-fullerene family with a diameter range between 4 and 25 nm [1], [2]. OLCs have a spherical shape with concentric layers of nano-graphitic sheets of carbon atoms [3]. There is a diversity of methods to synthesize OLCs and these include ion implantation, counterflow diffusion flames, annealing of nano-diamonds, arc discharge, plasma atomizer of nano-diamonds, chemical vapor deposition (CVD), electron beam irradiation and flame pyrolysis (FP) [2], [4], [5]. The synthesis method of OLCs influences the properties of the OLCs [6]. Of all the synthesis methods for the OLCs, the flame pyrolysis method is the most preferred because it does not utilize increased amounts of energy, is a catalyst-free method and is cost-effective [7]. The flame pyrolysis synthesis method uses a single-step process that uses hydrocarbon sources that are not too expensive and produces greater yields of OLCs [5]. OLCs have attracted much attention due to the variety of properties they possess. In addition to the high surface area to volume ratios, low densities, graphitic multilayer morphologies, biocompatibility, low toxicity, high thermal stability, and increased conductivity, this material has several other properties [5]. The properties of OLCs make them good contenders for various purposes such as catalysis, energy storage and conversion, water treatment, and biomedical applications [8].

In this study, the flame pyrolysis method was used to synthesize OLCs. A diversity of starting materials (hydrocarbons) has been explored to successfully synthesize OLCs using the flame pyrolysis method. Mongwe *et al.*, [9] used olive oil to produce OLCs. Sikeyi *et al.*, used olive oil [5], coconut oil [10], and thiophene [11] to produce OLCs. B. Shaku *et al.*, used grapeseed oil [12] to form OLCs. While these studies produced high-quality OLCs materials, they used pure oils, which will hinder large scale production of OLCs due to high cost. In this study, we explored the use of waste engine oil as a precursor for the synthesis of OLCs.

About 20% of engine oil is used in a motor vehicle before it is removed while 80% of engine oil is discarded as waste [13]. The removed engine oil is referred to as “waste” oil because with time, the oil starts to break down. The waste engine oil is produced by any impurities such as

(i) powdered metals, (ii) sulphur, (iii) water, (iv) carbon, and ash[14]. These alter the chemistry and affect the properties of the engine oil, which is harmful to the environment. Thus, it is important to recycle waste engine oil to prevent environmental contamination [14]. The composition of the waste engine oil used in this study is expected to influence the results. How the catalyst performs may be affected by the impurities present in the waste engine oil. Some of the impurities are removed from the process of pyrolysis when making the OLCs. In this chapter OLCs were synthesized, functionalized with nitric acid and doped with melamine as the nitrogen source.

4.2 Materials and methods

4.2.1 Chemicals

Waste engine oil (local mechanic), 55% Nitric acid (HNO_3) and Melamine were purchased from Merck South Africa. All chemicals were of analytical grade and were used without further purification.

4.2.2 Experimental procedure

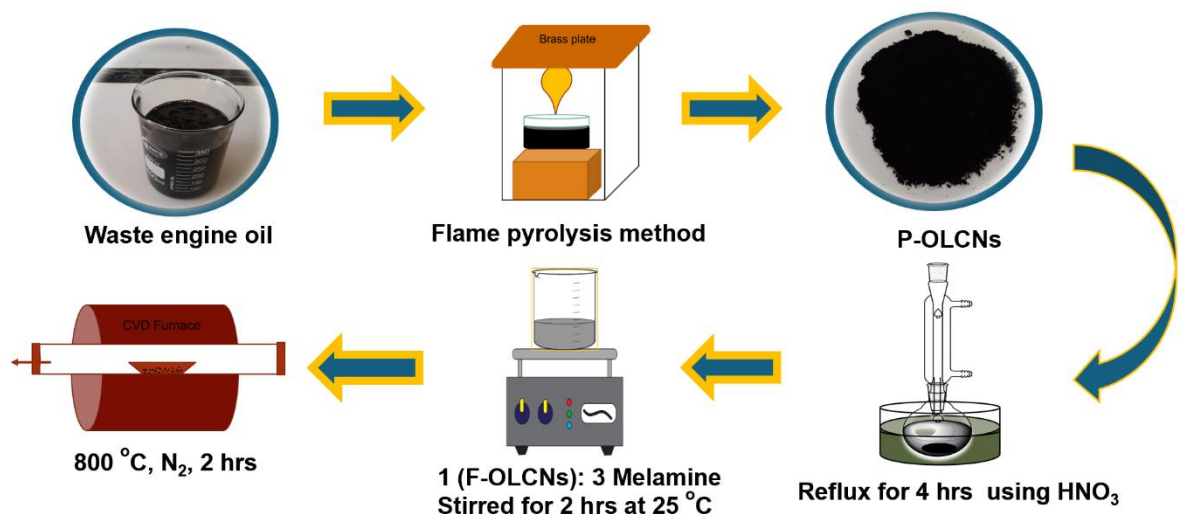


Figure 4.1: Shows the schematic diagram of the synthesis of the OLCs.

a. Synthesis of OLCs

OLCs were synthesized over a flame pyrolysis of waste engine oil as reported in the literature [5], [9], [15]. In a standard procedure, a wick was submerged in 200 mL of waste engine oil. The wick was then kindled to produce a flame. A pitch-black powder was formed due to the

burning of the oil in the central area of the flame. The powder was allowed to accumulate onto a brass collecting plate (BCP) placed about 30 mm above the flame for 2 hours. The collected black carbon powder (3.47% yield) was named pristine onion-like carbons (p-OLCs). Equation 4.1 (appendix) shows the calculation of the percentage yield.

b. Purification and functionalization of p-OLCs

The purification of pristine onion-like carbon (p-OLCs) was done by using 2 M HNO₃ [16]. In a standard experiment, p-OLCs (3 g) were added to a round bottom flask with 50 mL of 2 M HNO₃. The amalgamation was refluxed for 4 hours. The resulting acidified onion-like carbon mixture was removed using a centrifuge for 20 minutes and washed with double distilled water until a neutral pH was achieved. This was dried in an oven at 100 °C overnight to obtain the F-OLCs.

c. Doping of F-OLCs using melamine

A ratio of 1:3 of F-OLCs to Melamine was stirred in 35 mL of deionized water for 2 hours at room temperature. The mixture was allowed to dry in the oven at 80 °C for 24 hours. The dried sample was placed in a quartz tube which was placed in a CVD reactor. Doping was achieved at 800 °C under the flow of nitrogen for 2 hours. The resulting sample was named N-OLCs.

4.3 Characterization of the OLCs

Fourier transform infrared spectroscopy (Bruker Vector 22 FT-IR spectrometer) was employed to identify the functional groups present in the waste engine oil. The crystallinity and interlayer spacing of the synthesized OLCs were assessed using Powder X-ray Diffraction (XRD) Bruker D2 phaser with monochromatic Cu K α radiation, characterized by a wavelength of $\lambda = 0.1505$ nm, produced at 30 kV and 10 mA. The diffraction peaks were compared to those of standard carbon materials from literature references, using the EVA software package within the diffraction plus evaluation package for analysis. The T6400 Raman spectrometer from HORIBA scientific under Jobin Yvon Technology was used to analyse the quality of the onion-like carbon materials and identify structural changes within the p-OLCs, F-OLCs, and N-OLCs. The morphology of the OLCs was determined using a JEOL JEM 2100 transmission electron microscopy (TEM) operating at 200 kV. The instrument was coupled with a Thermo Fischer detector for EDS. The Zeiss Sigma 03-39 Fe-scanning electron microscopy (SEM) was used

to analyze the external morphology of the synthesized OLCs. The thermal stability of the OLCs was determined using the Perkin Elmer 6000 thermogravimetric analyser (TGA). The Brunauer, Emmett and Teller (BET) surface area and porosity were determined using a Micromeritics Tristar 3000 surface area and porosity analyser.

4.4 Results and Discussion

4.4.1 Fourier Transform Infrared Spectroscopy

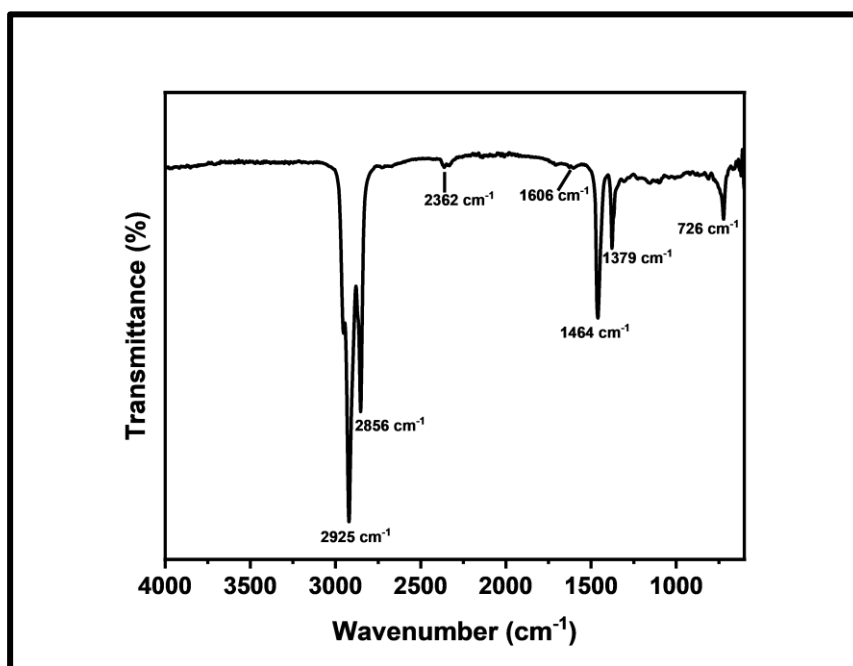


Figure 4.2: The FTIR spectrum of the waste engine oil used to synthesize the OLCs.

Fourier Transform spectroscopy was used to analyse the chemical composition of the waste engine oil used in this study. The peaks assigned at 2925 cm^{-1} and 2856 cm^{-1} on the FTIR spectrum are indicative of the presence C-H groups characteristic of alkane functional groups [17]. The weak peak observed at 2362 cm^{-1} is likely attributed to the C=C stretch, a characteristic feature of carboxylic acids[17]. However, the absence of additional signals, such as C-O peaks suggest the lack of other groups typically associated with carboxylic acids. The faint peak at approximately 1606 cm^{-1} can be associated with the N-H group, a characteristic feature of amines. These amines serve as part of the antiwear additive present in the engine oil [18]. The peaks assigned to 1464 cm^{-1} and 1379 cm^{-1} are attributed to the -CH₃ groups [17]. The peak at 726 cm^{-1} comes from the C=C bonds typically found in aromatic structures [17], [18], [19]. Table 4.1 shows the summary of the functional groups present in the waste engine

oil. From the above analysis the waste engine oil from the local mechanic is composed of hydrocarbons, aligning with expectations. However, it is important to note that the waste engine oil is tainted by a combination of chemical and physical impurities stemming from the friction between the engine components in various motors [19]. Additionally, these contaminants result from oxidation induced by increased temperatures within the engine [20].

4.4.2 Powder X-Ray Diffraction

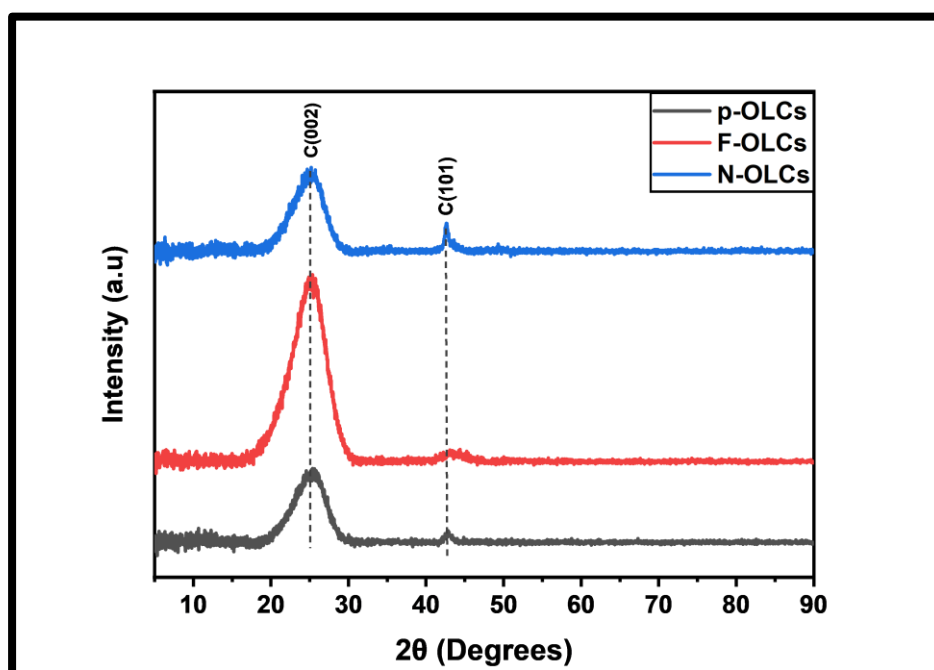


Figure 4.3: The PXRD patterns of the synthesized OLCs.

Figure 4.3 shows the PXRD patterns of the synthesized p-OLCs, F-OLCs, and N-OLCs. The diffraction peaks for the p-OLCs, F-OLCs, and N-OLCs within the ranges $25.0 - 25.3^\circ$ and $42.8 - 43.6^\circ$ are attributed to the (002) and (101) planes, respectively. The slight shift of the 2θ values is due to the purification and doping of the OLCs. The respective OLC materials showed two intrinsic peaks which are ascribed to a graphitic carbon structure and the peaks at around 25° are attributed to sp^2 carbons [21]. The peak observed in the XRD pattern for the F-OLCs showed an increased intensity when compared with the peaks of both p-OLCs and N-OLCs. The increased intensity potentially stemmed from the generation of defects during the functionalization and purification process during synthesis, wherein additional oxygen groups were introduced on to the carbon structure's basal plane [22]. Different synthesis methods of

OLCs result in a variety of interlayer spacings. The interlayer spacings for p-OLCs, F-OLCs, and N-OLCs were found to be 0.35 nm, 0.36 nm, and 0.35 nm, respectively (shown in equation 4.2 in the appendix). The interlayer spacing for p-OLCs and N-OLCs in this study was found to be 0.35 nm, which matches the interlayer spacing observed in OLCs synthesized using a heating/pyrolysis method with ultra-disperse diamond as the carbon precursor[23]. The F-OLCs interlayer spacing has no significant difference compared to the p-OLCs and N-OLCs. During the doping process of F-OLCs, the oxygen groups are replaced by nitrogen groups, consequently reducing the interlayer spacing.

4.4.3 Raman Spectroscopy

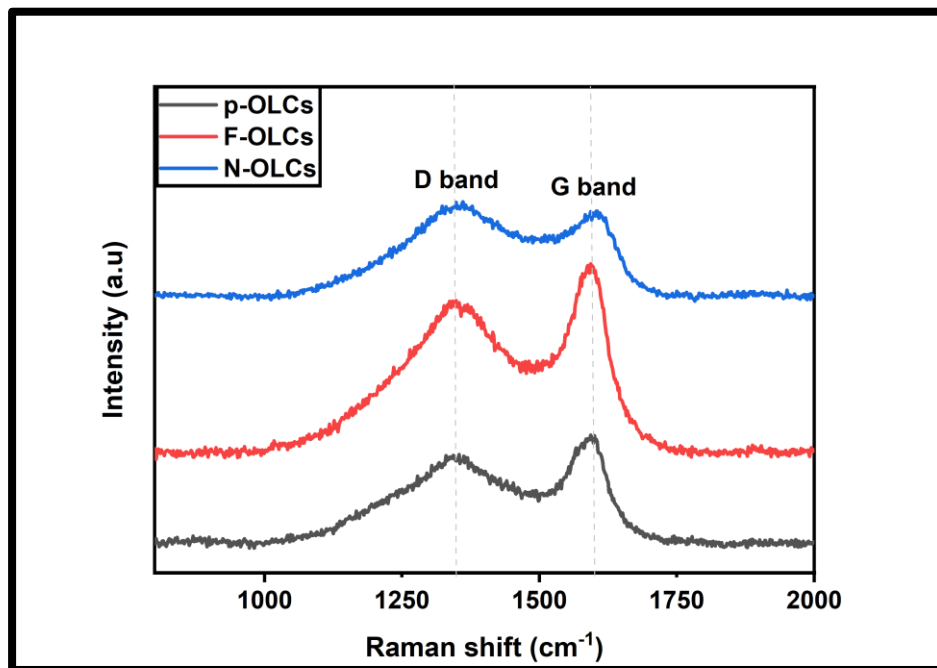


Figure 4.4: The Raman spectra of the synthesized p-OLCs, F-OLCs, and N-OLCs.

Raman spectra indicate that there is a slight return of the N-OLCs to the p-OLC spectrum instead of an improvement of F-OLC. This data is confirmed by the XRD results i.e., the return of N-OLC to p-OLC. The spectra in Figure 4.4 displays two eminent peaks: the D band and G band for the p-OLCs, F-OLCs, and N-OLCs, respectively. The peak positions and A_D/A_G ratios are summarized in Table 4.2. The Area of the D and G bands were used to calculate the A_D/A_G ratio using the Lorentz expression to fit the Raman Spectra. The peaks observed from $1347.0 \text{ cm}^{-1} - 1357.7 \text{ cm}^{-1}$ are assigned to the D band. The D band reacts to imperfections and disarray in the structure, which are correlated with doping [24]. The peaks observed from $1587.0 \text{ cm}^{-1} - 1591.6 \text{ cm}^{-1}$ are attributed to the G band which is a result of the stretching vibration of the

structured sp^2 bonded carbon atoms in the plane corroborated by the XRD analysis [24]. The higher the A_D/A_G ratio the more defects and imperfections the OLC nanoparticles will have [25]. The summary in Table 4.2 indicates that the N-OLCs possess an increased A_D/A_G ratio implying an increased number of defects present in the material due to doping of the F-OLCs using melamine as the nitrogen source. The N-OLCs low 2D band peak intensity demonstrates how substitutional nitrogen components doping has permeated the OLCs [26]. It is interesting to note that the Raman peaks for the F-OLCs have an increased intensity, like the XRD peaks for the F-OLCs. This may be due to the F-OLCs being more polarized, which would increase the intensity of the Raman signal [27]. This polarization may be due to the addition of oxygen groups to the OLCs.

Table 4.1 Summary of Raman data

	D Band		G Band		
Sample	Raman shift (cm^{-1})	Area	Raman shift (cm^{-1})	Area	A_D/A_G Ratio
p-OLCs	1347.0	245201.6	1587.0	89831.1	2.73
F-OLCs	1350.1	425014.7	1588.3	159650.6	2.66
N-OLCs	1357.7	261521.9	1591.6	82005.1	3.19

4.4.4 Transmission electron microscopy

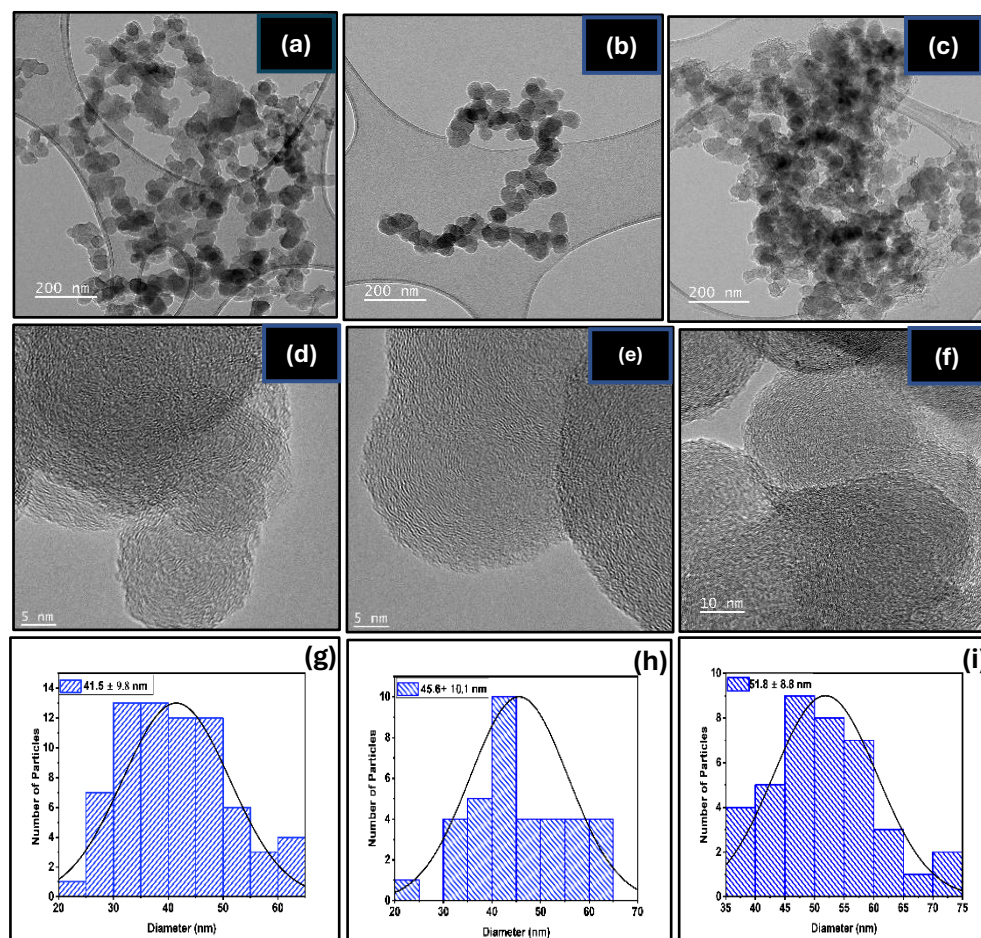


Figure 4.5: TEM images of (a) & (d) p-OLCs, (b) & (e) F-OLCs, (c) & (f) N-OLCs, Particle size distribution of (g) p-OLCs, (h) F-OLCs, and (i) N-OLCs.

The morphology of the as-synthesized p-OLCs, as shown in Figure 4.5 (a) and (d), exhibits almost a spherical coaxial morphology with chain-like interactions between the individual spherical p-OLC particles. This is a characteristic feature of OLCs, Ramaya *et al.*[28], Sikeyi *et al.*[16], [29], [30], Mongwe *et al.*,[31], [32], and Ntuli *et al.*, [33] observed a similar morphology from the synthesized OLCs. The average diameter of the synthesized p-OLCs was found to be 41.5 ± 9.8 nm as shown by the particle size distribution plot in Figure 4.5 (g). The morphology of the F-OLCs is shown in Figure 4.5 (b) and (e). The F-OLCs also show a spherical coaxial morphology and maintained the chain-like interaction. The purifying and functionalization process did not alter the morphology of the OLCs. The average diameter of the F-OLCs is 45.6 ± 10.1 nm as shown in Figure 4.5 (h) from the particle size distribution. The morphology of the N-OLCs is shown in Figure 4.5 (c) and (f). The first thing observed is

that the N-OLCs are agglomerated and maintain the chainlike interaction. The N-OLCs exhibit a distorted spherical morphology which may be attributed to the substitution of the nitrogen components. The average diameter of the N-OLCs was found to be 51.8 ± 8.8 nm. The increased particle size distribution in N-OLCs is attributed to the following: Firstly, doping which was achieved using melamine at 800 °C. At higher temperatures, OLCs are reported to coalesce, which results in bigger particles [34]. Secondly, since there was no purification step to get rid of excess oil from the OLCs (i.e. extraction), residual oil could result in further formation of OLCs, which will increase the size of the existing materials [34]. The N-OLCs appear to be more defective compared to the p-OLCs and F-OLCs and this is a result of the disruption of the carbon arrangement stimulated by nitrogen doping [22]. As more functional groups were added, the diameter of the OLCs increased. The BET surface area of the synthesized OLCs is summarized in Table 4.2. The BET surface area of p-OLCs is slightly lower than that of F-OLCs, which could be attributed to the presence of excess oils from the precursor, hindering nitrogen adsorption. The significant increase in BET surface area of N-OLCs is attributed to the defects associated with nitrogen-doping. This was also observed by other researchers, and it is consistent with literature [12] , [16]. This demonstrates that the functionalization and doping promote nitrogen adsorption, resulting in increased surface area.

Table 4.2 Summary of the BET surface area analysis of the OLCs.

Sample	Surface Area (m²g⁻¹)	Pore Volume (cm³g⁻¹)	Pore size (nm)
p-OLCs	55.2	0.0883	6.07
F-OLCs	60.2	0.130	8.64
N-OLCs	134	0.202	6.04

4.4.5 Scanning Electron Microscopy and Energy dispersive X-ray Spectroscopy

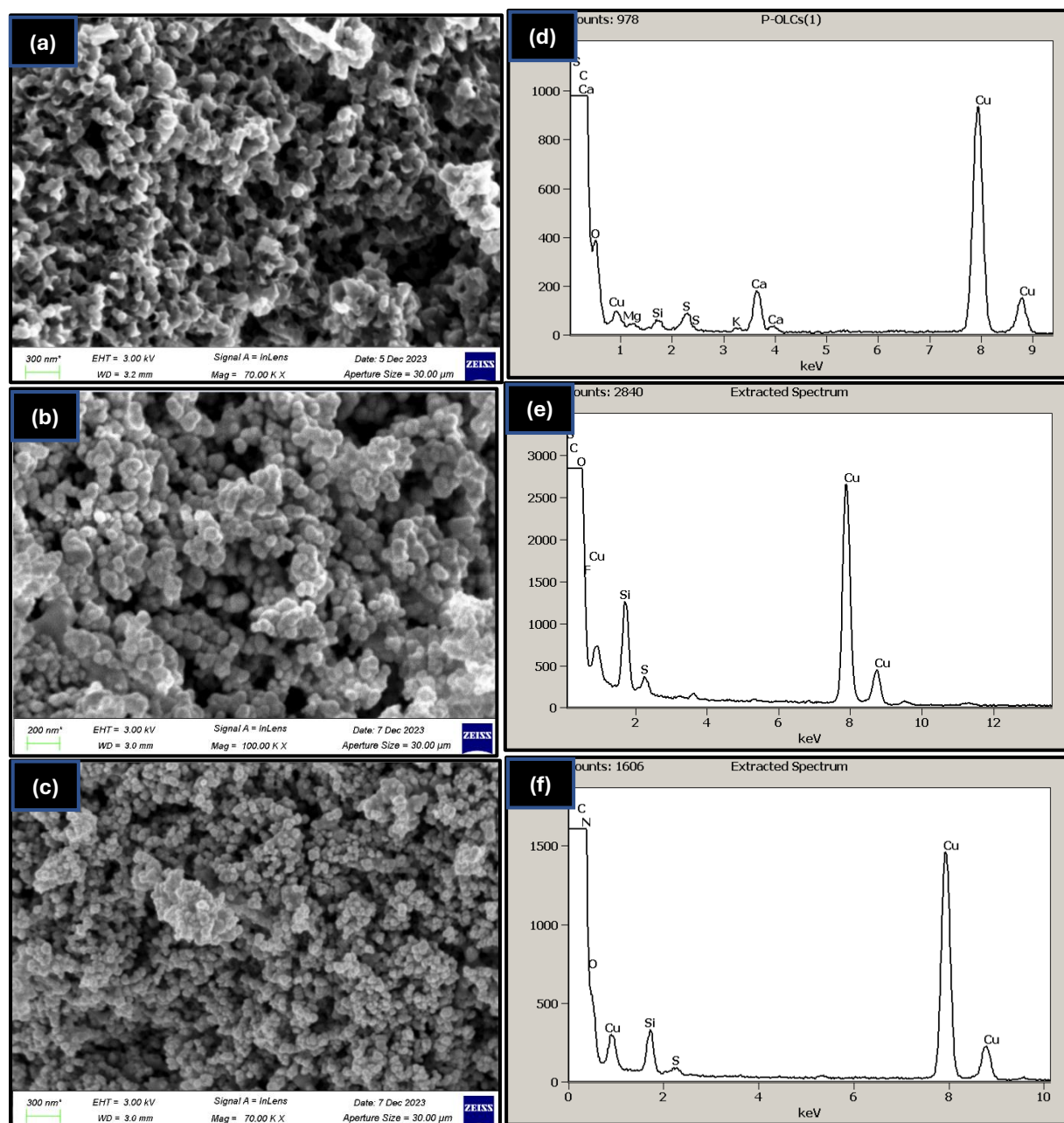


Figure 4.6: Displays SEM and EDS images of (a) and (d) p-OLCs, (b) and (e) F-OLCs, (c) and (f) N-OLCs, respectively.

The SEM images are demonstrated in Figure 4.6 (a) p-OLCs, F-OLCs, and (c) N-OLCs which show the interconnected chain-like interaction as seen in the TEM images in Figure 4.5 (a) p-OLCs, F-OLCs, and (c) N-OLCs. The SEM images reveal that the onion-like carbon particles are not hollow; instead, they comprise spherical shapes consisting of carbon atoms [35]. These

OLCs aggregate and form clusters. The SEM data is consistent with the TEM data. The EDS data for the p-OLCs (Figure 4.6 (b)) indicate the presence of S, C, Cu, Mg, Si, K, and Ca. The Mg, S, K, and Ca may be attributed to the metals present in the waste engine oil. This originated from the motor wear as well as the fuel [36], [37]. The presence of Cu is attributed to the Cu grid used for the analysis. The sample preparation for the EDS analysis was done on a copper grid. It is noted that following the purification and functionalization of the p-OLCs, the F-OLCs display increased oxygen content and most of the impurities have been eliminated during the purification process. Purification and functionalization of carbon materials using HNO_3 have been reported in the literature [16], [38]. Consequently, the EDS analysis confirms the functionalization of the p-OLCs. EDS confirms the presence of N, C and O after the doping of the F-OLCs (Figure 4.6 (e)) leading to the formation of N-OLCs (Figure 4.6 (f)). In addition, EDS confirms that there is no NH present which relates to the FTIR data already presented.

4.4.6 Thermogravimetric analysis

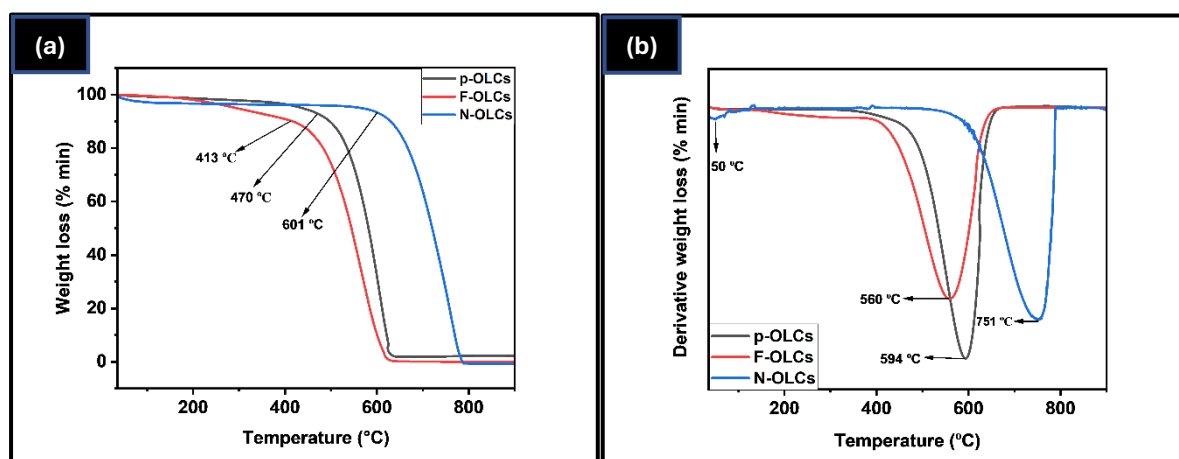


Figure 4.7: Displays the (a) Thermogravimetric analysis, and (b) differential thermogravimetric analysis of the synthesized OLCs.

The thermogravimetric and differential thermogravimetric analysis was conducted to determine the thermal stability of the p-OLCs, F-OLCs, and N-OLCs in Figure 4.7. The TGA curves (Figure 4.7 (a)) of the p-OLCs, F-OLCs, and N-OLCs show a great weight loss at 470 °C, 413 °C, and 601 °C, respectively. The reduction in the weight loss observed in F-OLCs at 413 °C is linked to the thermal breakdown of the oxygen functional groups, possibly involving parts of the carbon core within the onion-like structure [39]. The weight loss observed in the N-OLCs at 601 °C is ascribed to the removal of groups containing nitrogen and oxygen [16]. In

addition, the TGA of p-OLCs shows a slightly higher residual, compared to the F-OLCs and N-OLCs. This is consistent with the EDS data which showed other metal impurities in p-OLCs, which were subsequently removed through the purification process. The differential thermogravimetric data in Figure 4.7 (b) indicate that the N-OLCs demonstrated higher thermal stability at 751 °C than the p-OLCs (594 °C) and F-OLCs (560 °C). The higher thermal stability of N-OLCs is attributed to the incorporation of nitrogen atoms into the lattice of OLCs, forming disarranged materials as well as the larger particle sizes as shown by TEM images particle size distribution [16]. Figure 4.7 (b) displays a decreased weight loss peak for the N-OLCs at approximately 50 °C. This can be associated with the incorporation of nitrogen functional groups on the onion-like structure surface e.g. $C\equiv N$, $N^-=N^+=N^-$. The thermogravimetric and differential thermogravimetric analysis profiles have a consistent correlation with the Raman data. The p-OLCs synthesized from waste engine oil in this study exhibit the lowest thermal stability (594 °C) when compared to p-OLCs synthesized from various oils, such as olive oil (670 °C) [16], ghee oil (559 °C, 618 °C) [34], castor oil (721 °C), and paraffin oil (200 °C, 628 °C, and 668 °C) [40], as shown in Table 4.4. This disparity may be attributed to the fact that the above-listed studies used pure oils for the synthesis of p-OLCs using the flame pyrolysis method, while the current study utilized waste engine oil containing impurities, potentially contributing to the observed instability of the p-OLCs. It is noteworthy that when the OLCs in this study are doped with nitrogen, the thermal stability of the N-OLCs (751 °C) surpasses that of all doped and annealed OLCs. This suggests that recycling waste engine oil for OLC synthesis and subsequently doping it with nitrogen not only enhances stability but also proves to be a cost-effective alternative to purchasing pure oil for OLC synthesis. Ntuli *et al.*, used waste cooking oil to synthesize OLCs and the thermal analysis showed an individual decomposition step between 500 °C and 800 °C, which showed that the OLCs were thermally stable and contained no impurities which agree with the data found in this study [41]. Thermal analyses data of various OLCs synthesized using different oils in comparison to OLCs obtained in this study is shown in Table 4.3, which indicates that the most thermally stable materials are those synthesized using waste engine oil (i.e. the current study).

Table 4.3: Comparison of the thermal stability of synthesized OLCs using the flame pyrolysis method using different oils.

Sample	TGA (°C)	DTGA (°C)	Oil	Reference
p-OLCs	470	594	Waste engine oil	This work
F-OLCs	413	560	Waste engine oil	This work
N-OLCs	601	751	Waste engine oil	This work
p-OLCs	552	670	Olive oil	[16]
ox-OLCs	507	650	Olive oil	[16]
N-OLCs	534	710	Olive oil	[16]
p-OLCs	559	559,618	Ghee oil	[34]
ab ₁ OLCs	590	673	Ghee oil	[34]
ab ₂ OLCs	590	673	Ghee oil	[34]
ab ₃ OLCs	590	673	Ghee oil	[34]
p-OLCs	-	721	Castor oil	[40]
p-OLCs	-	200, 628, and 668	Paraffin oil	[40]

4.4.7 Conclusions

The OLCs were successfully synthesized using waste engine oil as the carbon source through the flame pyrolysis method. The addition of more functional groups onto the p-OLCs resulted in an increased surface area, as confirmed by both BET surface area analysis and the average diameter determined via TEM. Doping with melamine significantly enhanced the surface area, which is essential for effective catalysis. Previous literature has established that N-OLCs demonstrate superior performance in the electroactivity of ethanol oxidation, a finding observed by Sikeyi *et al.*, [16]. The N-OLCs were found to be thermally stable and with no impurities. The functionalization and doping of the OLCs were confirmed by EDS. This study revealed that N-OLCs have superior properties (high purity, BET surface area and thermal stability) necessary for alcohol oxidation than the functionalized and pristine OLCs.

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Chapter 5: Synthesis of WS₂ using the colloidal method

5.1 Introduction

Tungsten disulfide stands out for its intriguing electrocatalytic, electrochemical, and electronic properties within the vast landscape of TMDs [1]. These properties are associated with its special crystal structure, carrying covalently bonded S-W-S imitating a sandwich-like structure arranged in 2D sheets that are weakly interacted through van der Waals forces [2][3]. For this study, WS₂ is highly promising due to its unique chemical and physical properties stemming from the various characteristics of intralayer and interlayer bonding [4]. The properties of WS₂ include increased electronic conductivity, thermal conductivity, charge carrier mobility, stability, and adjustable bandgap [5]. Tungsten disulfide is a layered structure that has a plethora of oxidation states, prevailing redox active sites, solid electrolyte layers, increased surface area, electrochemical stability, and fast reaction rates [6]. The properties of WS₂ have attracted much attention for a variety of applications such as energy storage, supercapacitors, solar cells, biosensors, and lithium and sodium-ion batteries [7].

There are various methods used to synthesize WS₂ that control both the morphology and whether the material is layered or non-layered. These methods include (i) mechanical exfoliation, (ii) liquid phase exfoliation, and (iii) Li⁺ intercalation, and these are classified as top-down synthesis [8]. Another category of the synthesis of TMDs is the bottom-up synthesis and these include: (i) gas phase synthesis, (ii) hydrothermal method, (iii) microwave-assisted method, and (iv) colloidal synthesis method [9], [10]. The present colloidal synthesis method provides precise control over nanoparticle size, composition, and morphology, enabling the fabrication of tailored nanomaterials for a variety of applications [11]. In this study, WS₂ will be utilized as one of the components for the Pt-based composite, and the colloidal synthesis method, as performed by Gqoba *et al.*, was employed to synthesize WS₂ nanoflowers [9], [10]. The method was successful in producing WS₂ nanoflowers. The synthesis of WS₂ is known to be time-sensitive, and varying morphologies are observed at different reaction times. In particular, the nanoflowers were obtained after a reaction time of 45 minutes in this study.

5.2 Materials and methods

5.2.1 Chemicals

Oleylamine (OLA), thiourea ($\text{CS}(\text{NH}_2)_2$), tungstic acid (H_2WO_4), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), and hexane (C_6H_{14}) were acquired from Merk South Africa. All chemicals were of analytical grade and were used without further purification.

5.2.2 Experimental procedure

Figure 5.1 shows the schematic diagram of the synthesis of WS_2 . Oleylamine (10 mL) was degassed while constantly stirring at 120°C in a three-neck round-bottom flask [Figure 5.2 (a)]. Thiourea (0.12 g) was then added to the OLA, followed by tungstic acid (0.10 g) [Figure 5.2 (b)-(c)]. The temperature was rapidly increased to 320°C to facilitate the decomposition of the precursors, which is essential for the formation of WS_2 nanostructures. The reaction was maintained at this temperature for 45 minutes to allow the WS_2 nanostructures to grow. Figure 5.2 shows the different colour changes during the progression of the reaction of the synthesis of WS_2 . The amalgamation began boiling and transformed into a creamy yellow color around 150°C [Figure 5.2 (d)]. Thiourea decomposes at about 200°C and the reaction changed to a greyish and green colour [Figure 5.2 (e) – (f)]. As the reaction continued the colour changed to brown and eventually an ink black in colour [Figure 5.2 (g) – (h)]. Afterward, the reaction mixture was cooled for 5 minutes, and ethanol was added to isolate the colloids. The WS_2 nanostructures were collected via centrifugation and washed multiple times with ethanol/hexane (1:1) to remove excess OLA. The resulting black precipitate was dried at room temperature.

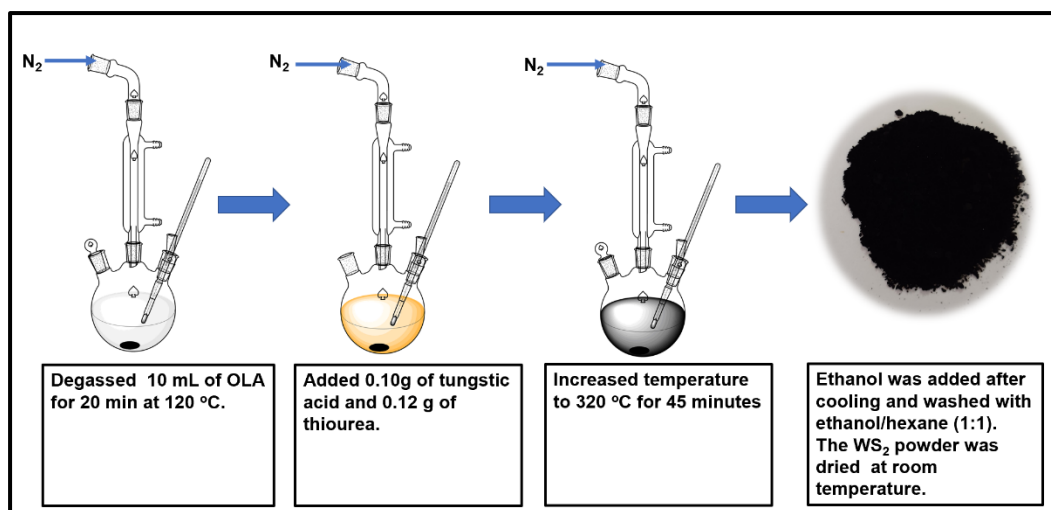


Figure 5.1: Schematic diagram of the synthesis of WS₂

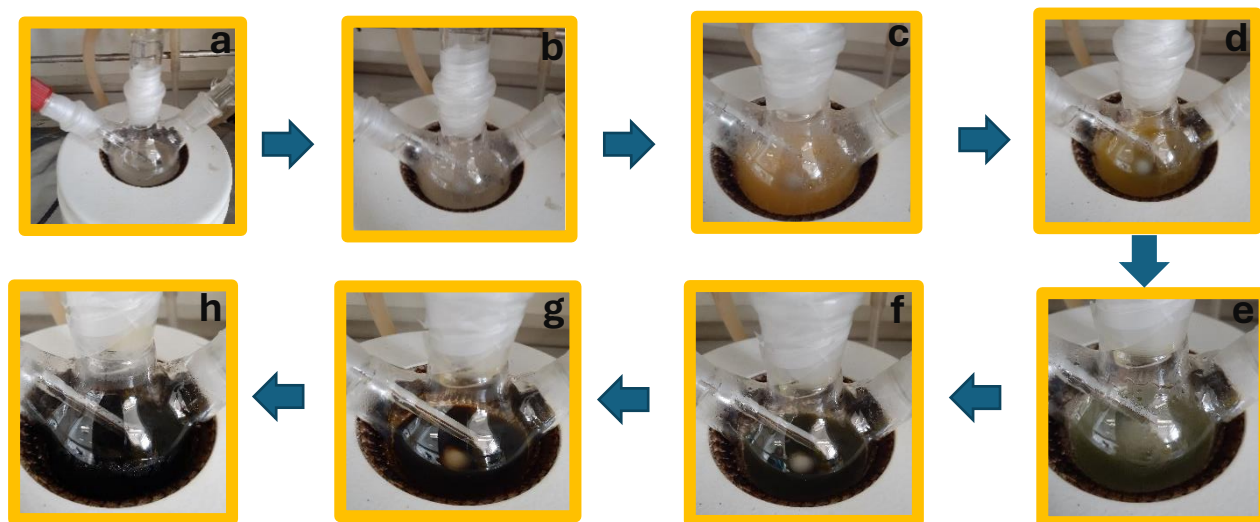


Figure 5.2: Images depicting various colour changes during the formation of WS₂.

5.3 Characterization of WS₂

The synthesized materials were characterised using XRD, TEM, SEM, EDS, Raman spectroscopy, and XPS, (See instrument specifications in Chapter 4).

5.4 Results and Discussion

5.4.1 Powder X-ray diffraction

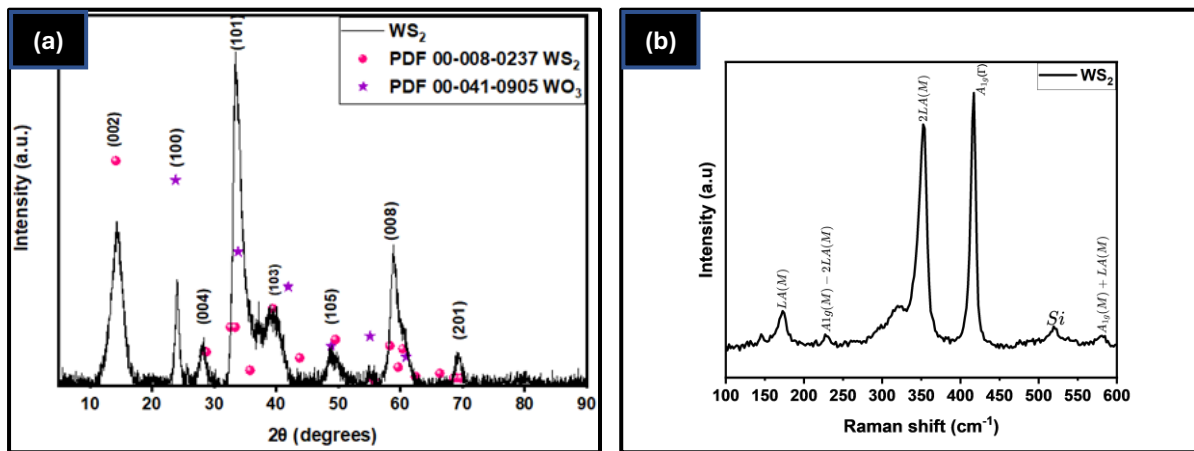


Figure 5.3: (a) XRD pattern and (b) Raman spectrum for the synthesized WS_2

Figure 5.3 (a) displays the XRD pattern of the synthesized WS_2 using the colloidal synthesis method, which was matched to the PDF file number 00-008-0237 (2H- WS_2). The peaks observed in the diffraction pattern align with the planes indexed as (002), (004), (101), (103), (105), (008), and (201). The major peaks observed at $2\theta = 14.3^\circ$ and $2\theta = 32.7^\circ$ correspond to the crystalline planes of (002) and (100), respectively [12]. This indicates that the synthesized WS_2 nanocatalyst has a hexagonal structure [13]. The intense broad peak at the (002) plane indicates the reduced size of the nanostructures, as well as the presence of multiple layers of WS_2 sheets [10]. The XRD pattern of WS_2 was also compared to the PDF file number 00-041-0905 (WO_3). It was noted that the XRD pattern of WS_2 had traces of WO_3 . The diffraction peak at about $2\theta = 24^\circ$ (★) is a result of the oxidation of WS_2 which forms impurities of WO_3 [10], [14].

Figure 5.3 (b) displays the Raman spectrum of the synthesized WS_2 . As observed from the Raman data, there are 2 prominent active modes which are assigned to the second order longitudinal acoustic $2LA(M)$ and out of plane $A_{1g}(\Gamma)$ vibrational mode of sulphur atoms found at 352 cm^{-1} and 417 cm^{-1} , respectively [15]. The Van der Waals intermolecular forces lead to a redshift in the $2LA(M)$ and $A_{1g}(\Gamma)$ modes, attributed to the diminishing interlayer interactions [9], [10], [16]. As the number of layers decreases, the intensity of the $2L(M)$ mode amplifies, whereas the behavior of the $A_{1g}(\Gamma)$ mode exhibits an inverse trend, diminishing in intensity [17]. However, we observe a slightly different trend from Figure 5.3 (b): the intensity of the

2L (M) mode is slightly lower than that of A_{1g} (Γ). This suggests that the synthesized WS₂ has an increased number of layers, as indicated by the decrease in the intensity of 2L (M) and the increase in the intensity of A_{1g} (Γ). An alternative way of confirming the layered structure of the synthesized WS₂ involves the notable decrease in intensity of the Si peak (519 cm⁻¹) with an increasing number of layers. This decrease is due to the growing number of layers, resulting in a steady weakening of the Raman laser hitting the Si surface, therefore causing a reduction in the Raman scattering intensity [18]. The intensities of the 2L (M) mode and A_{1g} (Γ) mode was used to determine the $I_{2L(M)}/I_{A_{1g}(\Gamma)}$ and it was found to be $\frac{I_{2L(M)}}{I_{A_{1g}(\Gamma)}} = 0.87$. The relative intensity $I_{2L(M)}/I_{A_{1g}(\Gamma)}$ ratio has been observed to increase significantly with a decrease in the number of layers from 2.2 to 0.47 at a wavelength of 514 nm [17]. When comparing the intensity of 0.87 obtained from our study to that reported by Berkdemir *et al.*, for CVD-synthesized WS₂, our result is between the bilayer (2L) and tri-layer (3L) WS₂, which they found to be 1.01 and 0.72, respectively. This confirms that the synthesized WS₂ is a multilayered structure that has not reached the bulk form. The Raman data correlates with the prominent (002) peak observed in the XRD pattern in Figure 5.3 (a) which confirms the multilayer WS₂ nanoflowers.

5.4.2 X-ray photon Spectroscopy

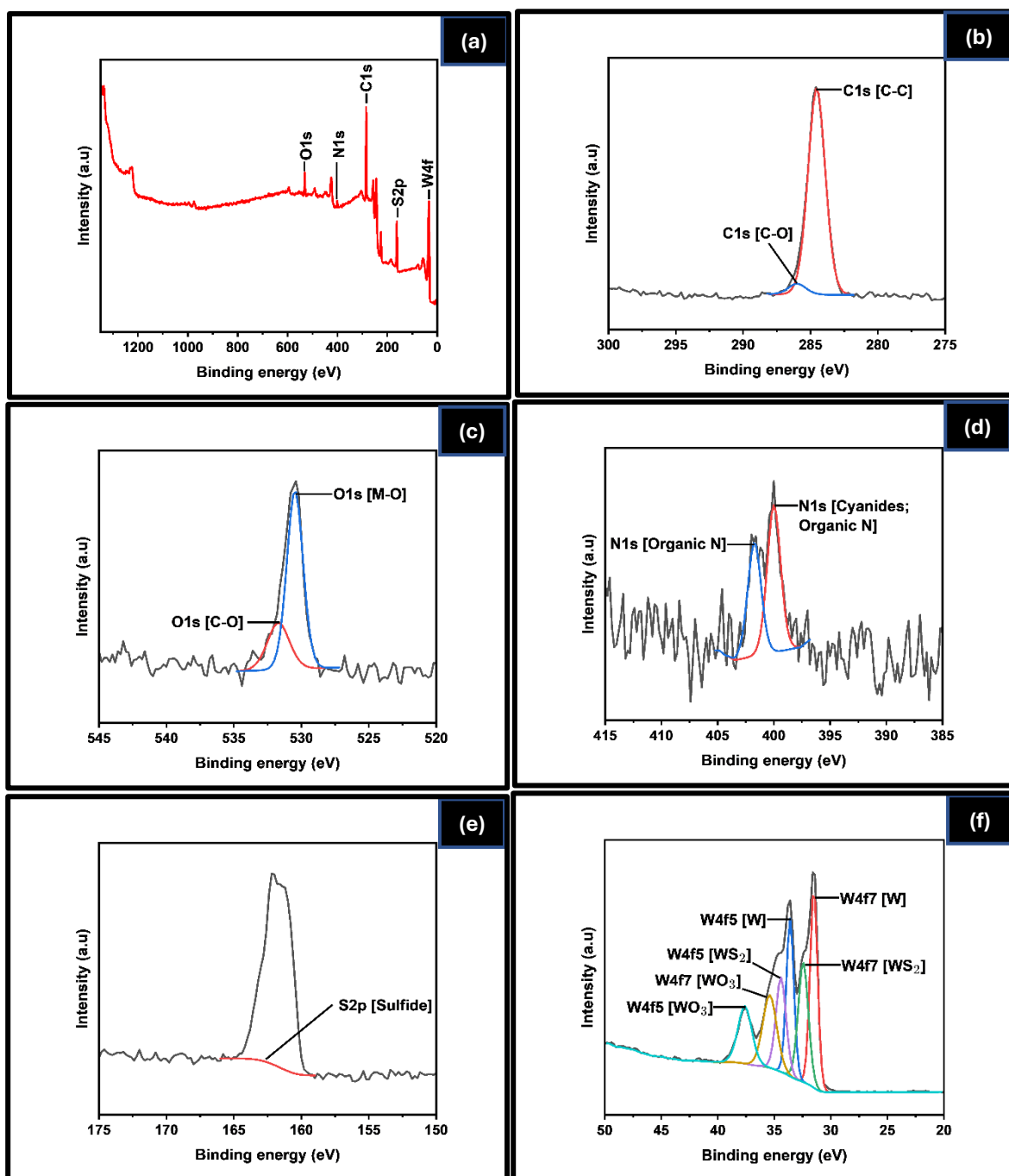


Figure 5.4: XPS spectra for the synthesized WS_2 .

The chemical phase and chemical composition of the WS₂ was determined by XPS studies [19]. The full survey spectrum of WS₂ synthesized at 45 minutes is displayed along with the core levels present in the material in Figure 5.4 (a). The high-resolution XPS spectra focus on O 1s, N 1s, C 1s, S 2p, and W 4f for the evaluation of the surface of the WS₂. An intense C 1s peak was observed which was attributed to the capping agent OLA that was used during the synthesis of WS₂. This serves as evidence for a considerable replacement of ligands originating from the capping agent, which is reflected in the strong C 1s signal obtained through XPS analysis[20]. A similar trend was observed in literature from Gqoba *et al.*, and other reported work in literature [9], [10], [20], [21]. Figure 5.4 (b) is a representation of the deconvoluted C 1s regional scan which demonstrates two distinct peaks associated with C-C and C-O molecular bonds. The C-C bonds result from OLA, while the C-O bonds result from the oxidation of OLA. Figure 5.4 (c) is a representation of the deconvoluted O 1s regional scan which demonstrates two distinct peaks associated with C-O and M-O molecular bonds, where M is a representation of a metal oxide. The possible metal in this case would be tungsten (W-O), due to the presence of WO₃ as discussed in XRD in Figure 5.4 (a). The oxygen is also attributable to the oxidation of the capping agent [9]. Figure 5.4 (d) is a representation of the deconvoluted N 1s regional scan which demonstrates two distinct peaks associated with organic N and cyanides which are a result of the OLA on the surface of the synthesized WS₂. Figure 5.4 (e) is a representation of the deconvoluted S 2p regional scan which demonstrates a single peak assigned to a sulfide. Figure 5.4 (f) shows the deconvoluted W 4f regional scan which gave rise to the following peaks: a weak doublet W 4f₅ and W 4f₇ assigned to WO₃, a strong doublet W 4f₅ and W 4f₇ assigned to W, and a medium doublet W 4f₅, and W 4f₇ assigned to WS₂. The peaks assigned to WS₂ give rise to the peaks assigned to W in WO₃ after partial oxidation during synthesis [22]. The data from the XPS confirms that WS₂ was synthesized and that traces of WO₃ were found due to partial oxidation occurring during synthesis. This data corroborates what was observed from XRD data in Figure 5.3 (a). Table 5.1 shows the summary atomic % composition, characterization, and assignments of the synthesized WS₂ material.

Table 5.1: Summary of the atomic composition and assignments from the fitting of the XPS spectra shown in Figure 5.4.

Element	Atomic %	Peak binding energy (eV)	Assignments
W	9.6	31.5	W
		32.4	WS ₂
		35.4	WO ₃
S	16.9	161.7	S ²⁻
C	62.6	284.5	C-C
		286	C-O
N	3.4	400	Cyanides
		401.7	Organic N
O	7.3	530.5	M-O (Metal Oxide)
		531.7	C-O

5.4.3 Transmission electron microscopy and Scanning electron microscopy.

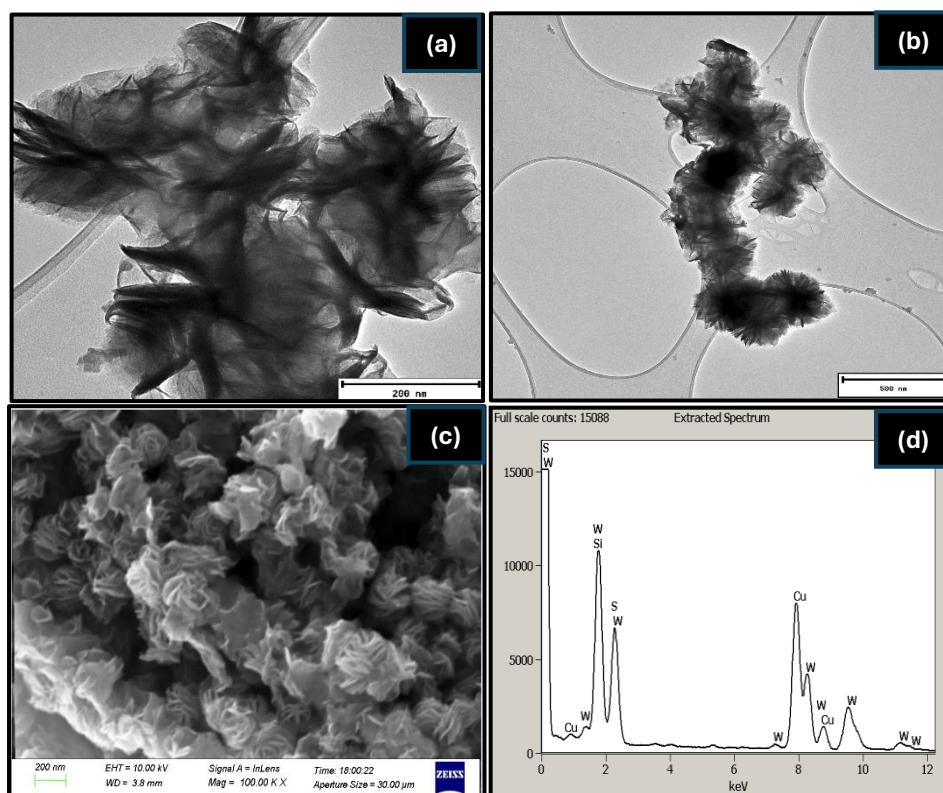


Figure 5.5: (a) – (b) Displays TEM images of WS₂ at different magnifications (c) SEM image of WS₂ , and (d) EDS of WS₂.

The morphology of the as-synthesized WS₂, as shown in Figure 5.5 (a) and (b), exhibits a nanoflower like morphology and they are connected [23]. The edges of the nanoflowers curled up with thin nanosheets and it is observed that the WS₂ is a layered structure. The SEM image is demonstrated in Figure 5.5 (c) which shows a consistent nanoflower morphology of the synthesized WS₂ which appears to be 3D and agglomerated. The flower-like morphology is known to donate an increased electrolyte-accessible surface area, hence an improved transfer resistance for the material occurs[12]. The flower-like morphology also increases the presence of the active sites thus enhancing the energy storage performance [12]. The EDS data for the WS₂ is shown in Figure 5.5 (d) and indicates the presence of W and S which is attributed to WS₂. The presence of Cu is attributed to the Cu grid used for analysis. The silicon observed from the EDS data could be due to silicon contamination from the glasswear used in the laboratory. It is observed from the EDS data that there is no presence of oxygen and WO₃ was observed in XPS. The reason for this could be that the traces of WO₃ were very small and the instrument was not sensitive enough to detect the oxygen peaks on the EDS.

5.4.4 Conclusion

The WS₂ nanoflowers were successfully synthesized through the colloidal method. The XRD pattern and the XPS confirmed the presence of WS₂ and traces of WO₃. The prominent (002) peak showed that the synthesized WS₂ is a layered structure and this was corroborated by the Raman data. The intensity ratio was found to be 0.87 and the prominent peaks were assigned to 2L (M) and A_{1g} vibrational modes.. The TEM and SEM images confirmed that nanoflower-like morphology was obtained at 45 minutes. The synthesized WS₂ nanoflowers will be used as a co-catalyst for the Pt-electrocatalyst in the subsequent chapters.

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Chapter 6: Synthesis of Pt supported on pristine, functionalised and nitrogen doped OLCs for direct ethanol fuel cells

6.1 Introduction

Direct ethanol fuel cells (DEFCs) have garnered significant focus over the years due to their advantages over other fuel cell technologies. However, their anode is known to perform poorly which is one of the factors that hinder the commercialization of DEFCs [1]. The favourable aspect about DEFCs is the use of ethanol which is a renewable fuel with low toxicity [2]. Although platinum is known for its good catalytic activity, it is not readily available and has poor extended stability [3]. Therefore, researchers have explored Pt-free electrocatalysts as an alternative [4], [5], [6]. Pt-free electrocatalyst have their challenges, including reduced activity and longevity in acidic mediums owing to low intrinsic activities and electrolyte degradation [3], [7]. As such, current research focuses on the use of supports, to reduce the Pt loading. For example, Li *et al.*, supported Pt on nitrogen doped C-Ni nanofibers and found that it was an adequate electrocatalyst for HER through electrospinning [8], [9]. In another study, Gwebu *et al.*, and Sikeyi *et al.*, supported Pt on TiO₂/carbon nanodots and TiO₂/S-OLCs, respectively [10], [11]. Both electrocatalysts displayed improved performance for the electrooxidation of ethanol and ammonia in alkaline media, respectively. These studies show that by carefully selecting a suitable support material, the performance of Pt electrocatalysts could be improved, while reducing the amount of the metal. In this study, we are taking advantage of the properties of the OLCs as support for the Pt electrocatalyst. OLCs qualify as one of the widely used carbon support in fuel cells due to (i) efficient conductivity [12], (ii) increased surface area [13], (iii) low density, (iv) biocompatibility, (v) high thermal stability, and (vi) low toxicity [7], [11], [14], [15], [16], [17]. Indeed, doping the carbon supports with heteroatoms is anticipated to enhance the performance of Pt-based electrocatalysts. For example, Sikeyi *et al.*, reported that supported Pd or Pt nanoparticles on doped OLCs improved the performance of the fuel cells compared to their undoped counterparts [11], [14], [17]. Studies by Kakei *et al.*, also demonstrated that Pd particles supported on doped reduced graphene oxide improved the performance of DEFCs [18].

In this study, the properties of pristine and modified OLCs are investigated for applications in alcohol fuel cells.

6.2 Materials and methods

6.2.1 Chemicals

Platinum acetylacetonate ($\text{Pt}(\text{acac})_2$), ethylene glycol ($\text{CH}_2\text{OH})_2$, ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), potassium hydroxide (KOH), and Nafion solution (5 wt.%) were purchased from Merck South Africa. All chemicals were of analytical grade and were used without further purification.

6.2.2 Experimental procedure

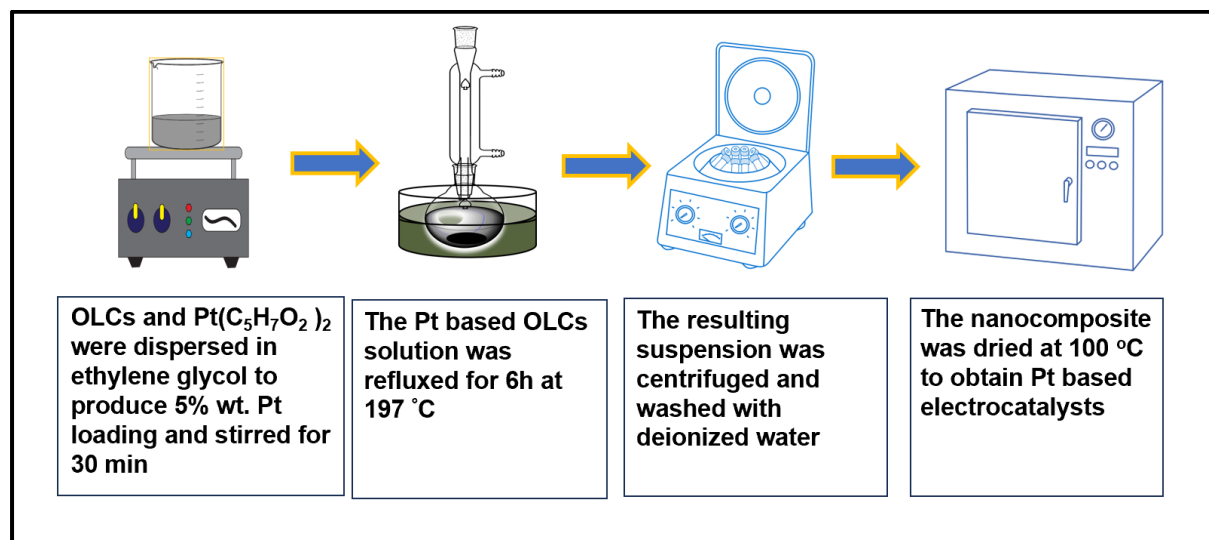


Figure 6.1: Shows the schematic diagram of the synthesis of Pt/p-OLCs, Pt/F-OLCs, and Pt/N-OLCs.

a. Synthesis of Pt-based OLCs

Synthesis of all electrocatalysts was achieved using a procedure reported by Sikeyi et al., [11], [17]. In a standard experiment, 200 mg of p-OLCs was dispersed in 20 ml ethylene glycol and a calculated amount of $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$ was added to produce a 5 wt.% of Pt loading under stirring for 30 minutes. The obtained mixture was sonicated in an ultrasound bath for 30 minutes at room temperature. The Pt/p-OLCNs nano catalyst solution was deposited into a round bottom flask and the solution was refluxed for 6 hours. The resulting suspension was centrifuged for 30 minutes and washed with deionized water until a neutral pH was achieved. The Pt/p-OLCs were dried at 100 °C overnight. This procedure was followed for the synthesis of Pt/F-OLCs and Pt/N-OLCs as shown in Figure 6.1.

6.3 Characterization of Pt/p-OLCs, Pt/F-OLCs, and Pt/N-OLCs

6.3.1 Physicochemical characterization

The synthesized electrocatalysts were analysed using XRD, Raman spectroscopy, XPS, TEM, SEM and EDS (See instrument specifications in Chapter 4).

6.3.2 Electrochemical characterization

a. Catalyst ink and glassy carbon electrode preparation

5 mg of the synthesized platinum-based electrocatalysts were added in 1 mL of ethanol and 5 μ L of Nafion solution to prepare the catalyst ink [19]. The catalyst ink was amalgamated through ultrasonication for 1 hour before being drop cast on a dried clean glassy carbon electrode (GCE). The GCE was polished using a figure 8 motion in a water-alumina slurry on a polishing pad to clean it [20].

b. Electrochemical measurements

The electrochemical measurements were done in a three-electrode cell at approximately 25 °C in an electrolyte solution of 1 M EtOH + 1 M KOH purged in argon for cyclic voltammetry for the electro-oxidation of ethanol. A Pt wire with an increased surface area was used as the counter electrode, and the Ag/AgCl (3.0 M KCl) was the reference electrode. The GCE electrode with a surface area of 0.196 cm² was used as the working electrode. The potential range for the cyclic voltammogram was -0.8 to 0.4 V at a scan rate of 50 mVs⁻¹ for 10 cycles.

6.4 Results and Discussion

6.4.1 Powder X-ray diffraction and Raman spectroscopy

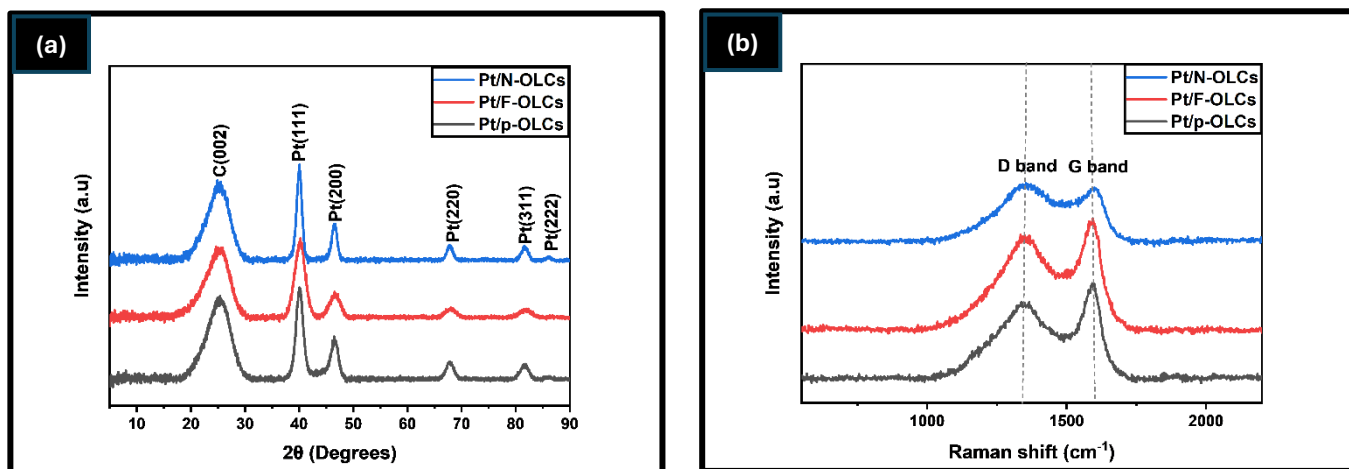


Figure 6.2: (a) PXRD pattern and (b) Raman spectra for the synthesized Pt-based electrocatalysts.

Figure 6.2 (a) shows the PXRD patterns of the synthesized Pt/p-OLCs, Pt/F-OLCs, and Pt/N-OLCs. All three samples show peaks at $2\theta = 25.3^\circ$, 40.1° , 46.4° , 67.8° , 81.6° , and 86.1° corresponding to the platinum miller indices with planes (111), (200), (220), (311), and (222) respectively with a face centred cubic crystalline structure (PDF file PDF 01-087-0647) shown in Figure 6.2 (a) [10]. The XRD pattern of the synthesized OLCs in Chapter 4 revealed the presence of the C (101) peak. The peak at $2\theta = 25.3^\circ$ is attributed to the carbon Miller indices (002). Additionally, the peak at $2\theta = 43.6^\circ$, corresponding to the Miller indices of C (101), disappears upon the incorporation of platinum. This is attributed to the shift in peak position, overlapping with the platinum peak at $2\theta = 46.4^\circ$ [21]. This is an indication that there is a structural change in the lattice of the OLCs due to the addition of Pt. The interlayer spacing of the different OLC supports was found to be approximately 0.35 nm. The F-OLCs had an interlayer spacing of 0.36 nm before the incorporation of Pt nanoparticles (see section 4). This confirms the structural change in the lattice of the OLCs after the addition of platinum, which is consistent with the literature [10], [14], [17]. The interlayer spacing of the Pt in Pt/p-OLCs, Pt/F-OLCs, and Pt/N-OLCs was calculated to be approximately 0.22 nm using the equation $d_{(hkl)} = \frac{n\lambda}{2\sin\theta}$. For the Pt/N-OLCs, a small peak with the Miller indices Pt (222) appears,

whereas it is not visible on Pt/p-OLCs and Pt/F-OLCs. The XRD data shows that Pt^{2+} was reduced to Pt and was interacting with p-OLCs, F-OLCs, and N-OLCs.

Figure 6.2 (b) shows the Raman spectra for the synthesized Pt/p-OLCs, Pt/F-OLCs, and Pt/N-OLCs. The Raman spectra display two eminent peaks: the D band and G band for the Pt/p-OLCs, Pt/F-OLCs, and Pt/N-OLCs, respectively. The peak positions and A_D/A_G ratio are summarized in Table 6.1. The area of the D and G bands was used to calculate the A_D/A_G ratio. The peaks observed from 1348.6 to 1351.1 cm^{-1} are attributed to the D band and the peaks observed from 1591.5 to 1596.6 cm^{-1} are assigned to the G band. The D and G bands are due to the presence of the OLCs, and it is noticeable that after the incorporation of Pt the D and G bands shift compared to the Raman peaks in Chapter 4. The D band displays a red shift due to the presence of the dispersive nature of Pt [22]. The shift in the D and G bands validates the addition of Pt on the Pt-based composites. The Raman spectra showed increased defects and disorders in the following order: Pt/p-OLCs < Pt/F-OLCs < Pt/N-OLCs. The Raman data is complementary to the XRD data shown above.

Table 6.1: Summary of Raman data.

	D Band		G Band		
Sample	Raman shift (cm^{-1})	Area	Raman shift (cm^{-1})	Area	A_D/A_G Ratio
Pt/p-OLCs	1348.6	270011.3	1595.2	95662.5	2.82
Pt/F-OLCs	1348.7	318574.3	1591.5	122631.8	2.60
Pt/N-OLCs	1351.1	202382.2	1596.6	66139.6	3.10

6.4.2 X-ray photon spectroscopy

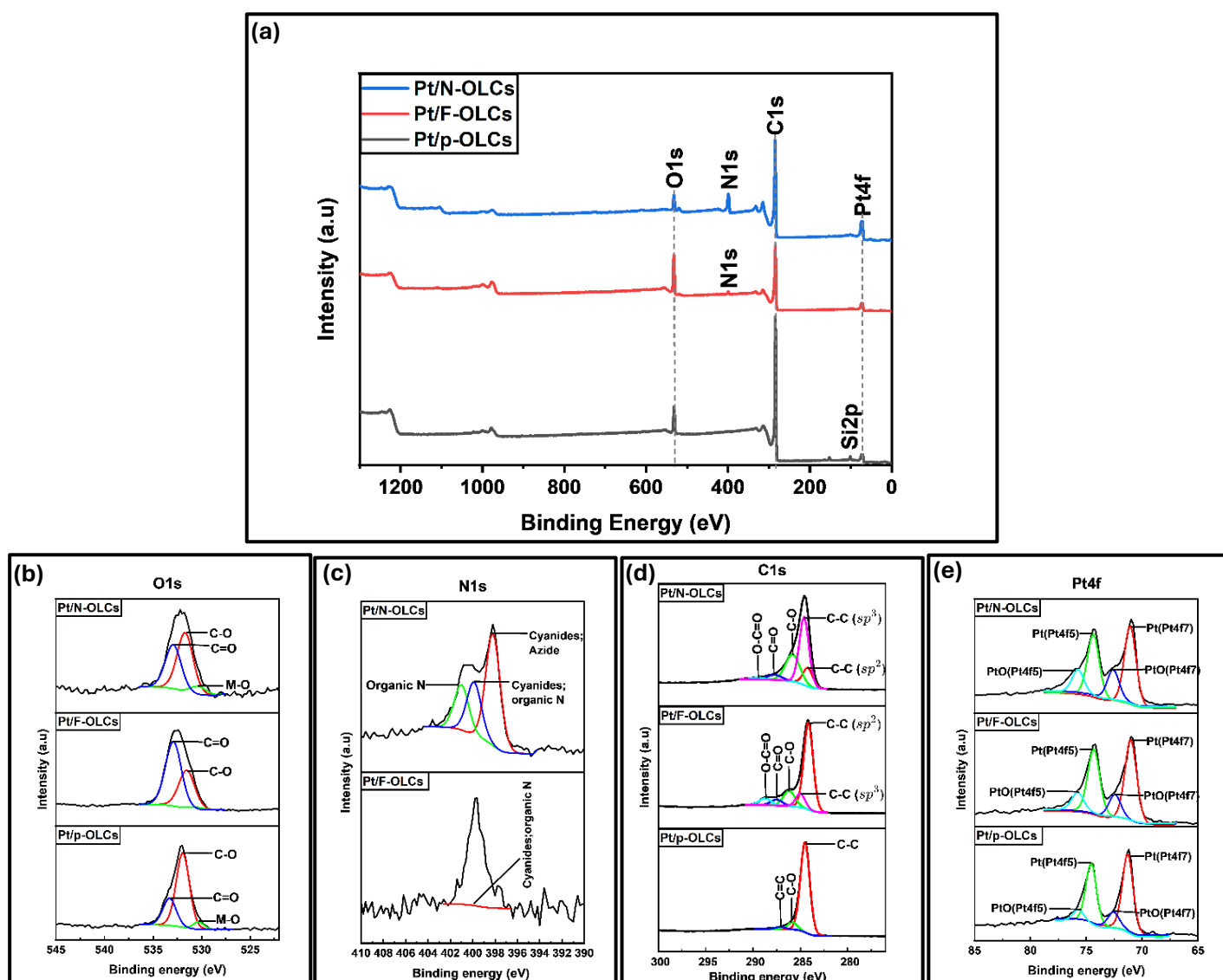


Figure 6.3: X-ray photon spectroscopy for the synthesized Pt-based electrocatalysts. (a) Survey spectrum (b) – (e) High-resolution spectrum of O 1s, N 1s, C 1s and Pt 4f.

The chemical phase and composition of Pt/p-OLCs, Pt/F-OLCs, and Pt/N-OLCs were determined by XPS studies. The full survey spectrum of the Pt-based electrocatalysts is shown along with the core levels present in Pt/p-OLCs, Pt/F-OLCs, and Pt/N-OLCs in Figure 6.3 (a). The high-resolution XPS spectra focus on O 1s, N 1s, C 1s, and Pt 4f for the evaluation of the surface of Pt/F-OLCs and Pt/N-OLCs. In the case of Pt/p-OLCs, there is the presence of Si 2p and the absence of N 1s. The Pt-based electrocatalyst common peaks at approximately 532 eV, 284 eV, and 73 eV are assigned to O 1s, C 1s, and Pt 4f, respectively. The Pt/F-OLCs have a

small peak at 399 eV, which is attributed to N 1s. This indicates that functionalizing with HNO₃ added nitrogen to the F-OLCs in small amounts, as shown in Table S2 in the appendix. For the Pt/N-OLCs, the small peak at approximately 399 eV is attributed to N 1s, confirming the doping of nitrogen in the Pt/N-OLCs. Shaku et al. reported that the N 1s peak was positioned at 398.9 eV, which is like the N 1s peak found in this work [23]. The deconvolution of the O 1s peak (Figure 6.3 (b)) for the Pt-based electrocatalysts produced oxygenated carbons C-O, C=O, and M-O, the Pt/F-OLCs had a very small peak for the M-O, where M is a representative of a metal (Pt). Figure 6.3 (c) is a representation of the deconvoluted N 1s regional scan which demonstrates a small single peak assigned to cyanides and organic N for the Pt/F-OLCs. The deconvoluted N 1s regional scan for the Pt/N-OLCs gave rise to peaks assigned to organic N, cyanides, organic N, and azides. Figure 6.3 (c) shows the deconvolution of the C 1s regional scan which produced 5 distinct peaks for the Pt/F-OLCs and Pt/N-OLCs. These peaks were assigned to O-C=O, C=O, C-O, C-C (sp²), and C-C (sp³) in aromatic rings [14]. The C 1s regional scan for the Pt/p-OLCs gave rise to 3 distinct peaks which are attributed to C=O, C-O, and C-C. It is interesting to note that functionalizing the OLCs introduces a new carbon group O-C=O which also increases the oxygen content. Figure 6.3 (e) shows the deconvoluted Pt 4f peaks for the Pt-based electrocatalyst which gave rise to the following peaks: a weak doublet Pt 4f₅ and Pt 4f₇ assigned to PtO and a medium doublet Pt 4f₅ and Pt 4f₇ attributed to Pt. This indicates the successful incorporation of Pt. The summary of the atomic composition and assignments from the deconvoluted spectra of the Pt-based electrocatalysts is shown in Tables S1, S2 and S3 in the supplementary data.

6.4.3 Transmission electron microscopy

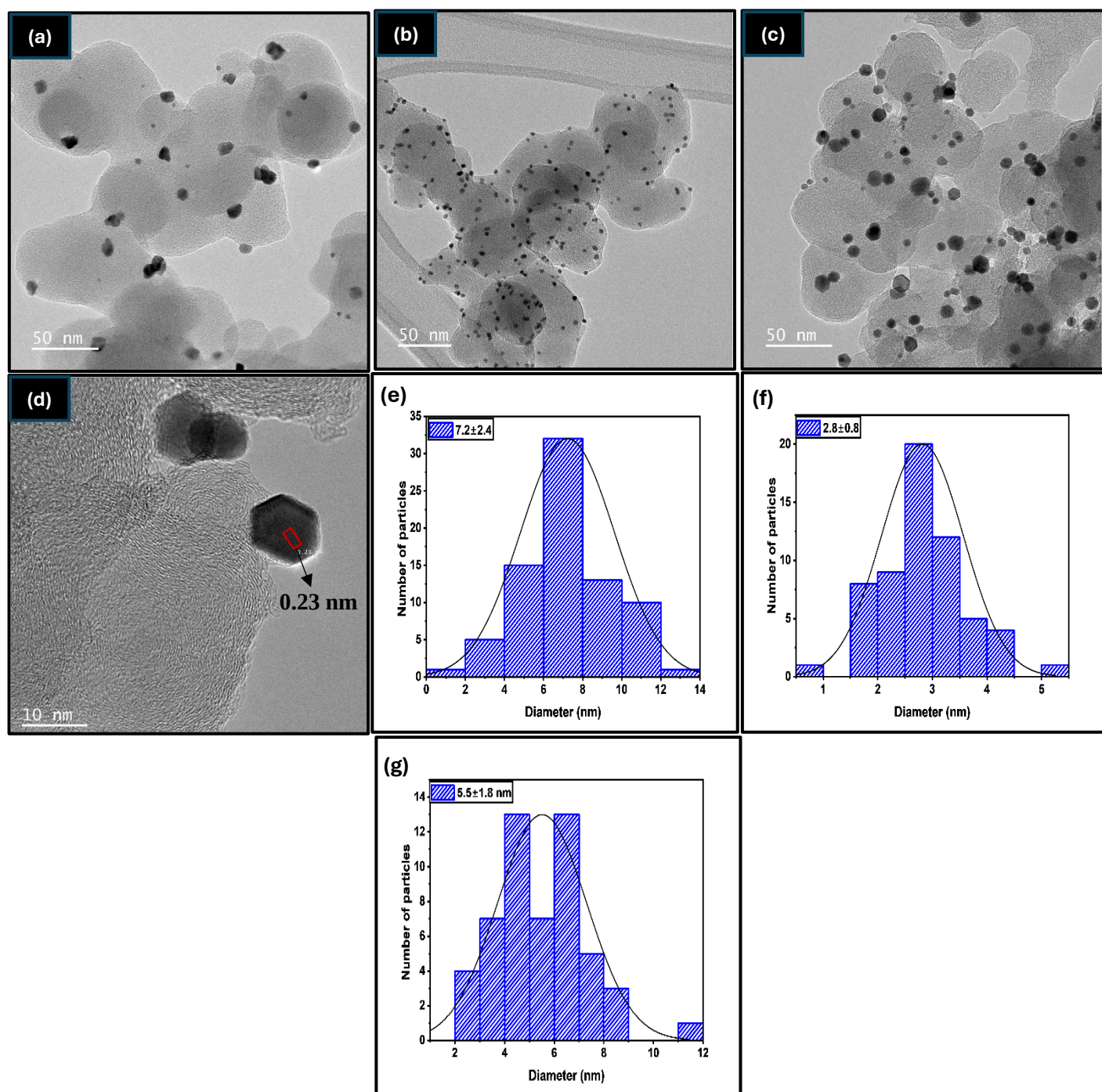


Figure 6.4: TEM images of (a) Pt/p-OLCs, (b) Pt/F-OLCs, (c) and (d) Pt/N-OLCs. Particle size distribution of (e) Pt/p-OLCs, (f) Pt/F-OLCs, and (g) Pt/N-OLCs.

The morphology of the synthesized Pt/p-OLCs, Pt/F-OLCs, and Pt/N-OLCs are shown in Figure 6.4 (a) to (c). The appearance of the nanoparticles on the p-OLCs, F-OLCs, and N-OLCs (Figure 6.4 (a) to (c)) confirms that platinum was successfully attached onto the OLCs.

The Pt nanoparticles in Figure 6.4 (a) on the p-OLCs are well dispersed, exhibiting an irregular shape with a larger average particle size of 7.2 ± 2.4 nm. What is captivating to observe is that when Pt nanoparticles are dispersed on p-OLCs, the shape of the p-OLCs becomes distorted. This distortion could be a result of structural disturbances introduced due to the addition of Pt. In Figure 6.4 (b), the Pt nanoparticles on the F-OLCs are well dispersed, appearing smaller in size and exhibiting a spherical shape compared to those on Pt/p-OLCs. The Pt particles in Pt/F-OLCs measure 2.8 ± 0.8 nm. In Figure 6.4 (c), the Pt nanoparticles on the N-OLCs are well dispersed, but there are a few clusters of nanoparticles on the surface of the N-OLCs. The Pt nanoparticles exhibit a mixture of spherical and hexagonal shapes, with an average particle size of 5.5 ± 1.8 nm. It is interesting to note that the doping of the OLCs with nitrogen alters the shape of the Pt nanoparticles. From the XRD data, we observe a face-centred cubic structure rather than a hexagonal crystal structure. Sikeyi *et al.*, loaded Pd onto N-OLCs and ox-OLCs, reporting that the Pd nanoparticles appeared larger and distorted on the ox-OLCs. [17]. This is contrary to what was observed in this study. For the N-OLCs, the Pd particles decreased in size, became spherical, and were highly dispersed. Kim *et al.*, loaded Pt onto N-OLCs, reporting that the Pt nanoparticles were highly dispersed with no agglomeration and had a small average particle size [25]. The nitrogen doping influenced the size and dispersion of the Pt nanoparticles, for the following reasons: (i) N-OLCs exhibit high electron densities due to the extra electron present in nitrogen compared to carbon, and (ii) nucleation sites are created in an increased area [26]. Both Sikeyi *et al.*, and Kim *et al.*, used NH_3 as the nitrogen source for doping the OLCs. In this study, melamine was used as the nitrogen source for doping the OLCs, which could be the reason for the change in the shape of the Pt nanoparticles. Both melamine and ammonia contain nitrogen, but melamine is organic while ammonia is inorganic. Figure 6.4 (d) shows the hexagonal Pt nanoparticle on N-OLCs with an interlayer spacing of 0.23 nm. Which is in agreement with the interlayer spacing derived from XRD of approximately 0.22 nm for all the synthesized Pt-based OLCs.

6.4.4 Scanning electron microscopy and energy dispersive spectroscopy

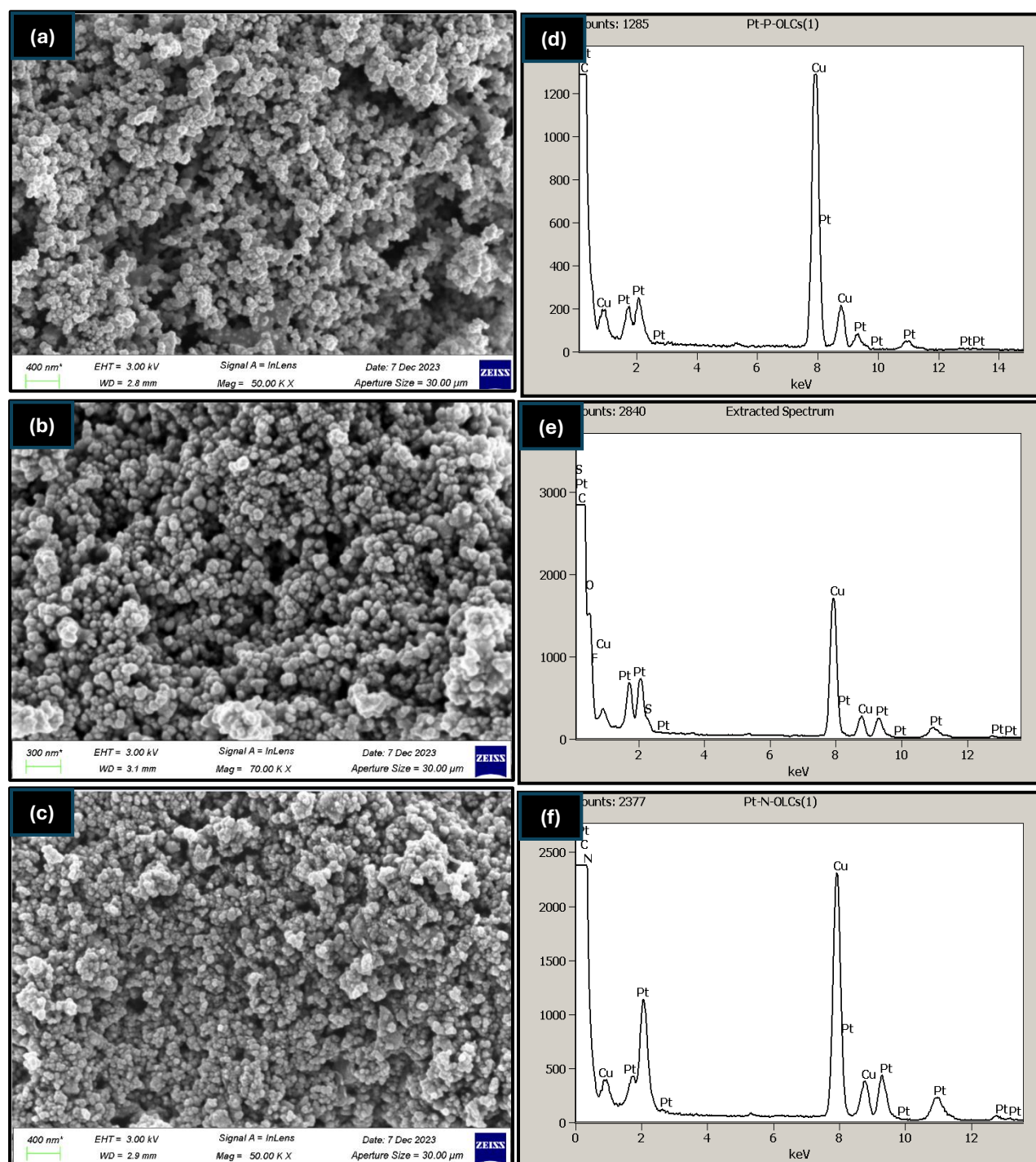


Figure 6.5: Displays SEM images and EDS of (a) and (d) Pt/p-OLCs, (b) and (e) Pt/F-OLCs, and (c) and (f) Pt/N-OLCs.

The SEM images are shown in Figure 6.5 (a) Pt/p-OLCs, (b) Pt/F-OLCs, and (c) Pt/N-OLCs which show the interconnected chain-like interaction which appears to be clustered. The

incorporation of Pt in the OLCs is confirmed by EDS shown in Figure 6.5 (d) Pt/p-OLCs, (e) Pt/F-OLCs, and (f) Pt/N-OLCs. Ethylene glycol removed sulphur (S), magnesium (Mg), silicon (Si), potassium (K), and calcium (Ca) from the p-OLCs during the synthesis of Pt/p-OLCs, as they were not detected in the EDS analysis. However, there is a possibility that these metals may still be present in trace amounts in the Pt/p-OLCs. The EDS data compliments the XPS by confirming the presence of Pt in the Pt-based composites.

6.4.5 Cyclic voltammetry of Pt/p-OLCs, Pt/F-OLCs, and Pt/N-OLCs

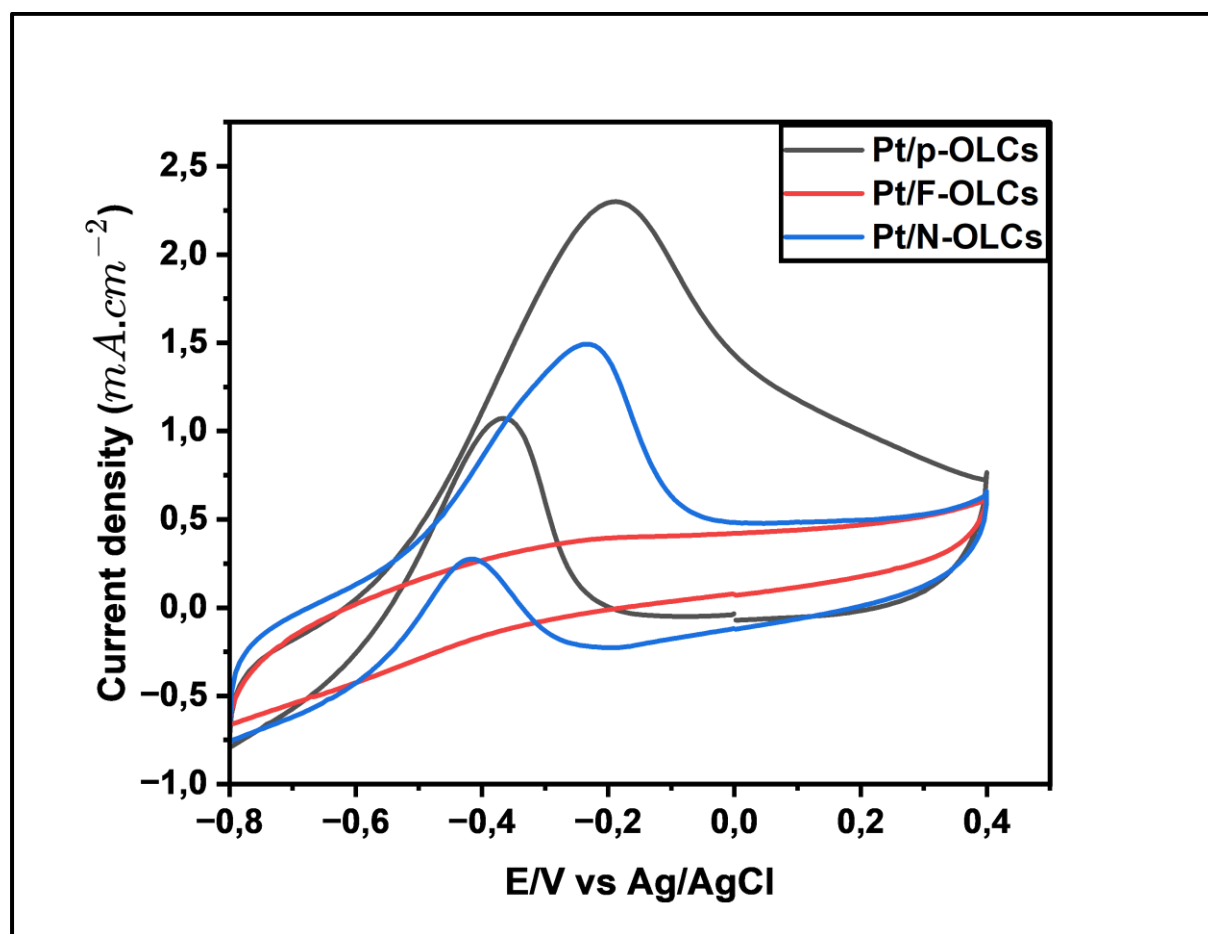


Figure 6.6: Cyclic voltammetry curves for Pt/p-OLCs, Pt/F-OLCs, and Pt/N-OLCs in 1 M KOH + 1 M EtOH solution at a scan rate of 50 mVs⁻¹.

Cyclic voltammetry was used to determine the electrochemical behaviour and the extent of poisoning to the synthesized Pt-based electrocatalyst [10]. The ethanol oxidation current peaks were observed during the anodic sweep, corresponding to the electrochemical processes occurring over the Pt surface in Figure 6.6. The current density for Pt/p-OLCs and Pt/N-OLCs

was found to be 2.3 mA/cm² and 1.5 mA/cm², respectively. However, Pt/F-OLCs did not exhibit an oxidation peak. This is an indication that Pt/F-OLCs did not oxidize the ethanol in the basic solution despite a well-dispersed Pt particles. The oxidation reaction is depicted by the forward peak because of chemisorbed species due to the adsorbed ethanol molecule [27]. In an alkaline medium, it is observed that the magnitude of the backward peak is diminished relative to that of the forward peak. This disparity stems from the enhanced ease of removing adsorbed carbonaceous species, facilitated by the presence of oxygen-containing and nitrogen-containing species, which accelerate the process of ethanol oxidation [19], [28]. The current density for Pt/p-OLCs was higher compared to that of Pt/N-OLCs. The reason for this could be that the p-OLCS still had traces of sulphur (S), magnesium (Mg), silicon (Si), potassium (K), and calcium (Ca). It is possible that the p-OLCs still contain trace amounts of the metals found in waste engine oil, whereas compared to the N-OLCs, the impurities have been removed through the process of purification and functionalization. From the XPS survey spectrum in Figure 6.3, it was observed that the survey spectrum for the Pt/p-OLCs consisted of traces of silicon (2p) (organic silicon), which consists of Si-C bonds. This form of silicon is known to be thermodynamically and kinetically stable due to the increased bond strength and reduced polarity of the bond [29]. The presence of Si in Pt/p-OLCs increased the conductivity of the composite thus improving the current density of Pt/p-OLCs [30]. Dong *et al.*, reported that Pt/SiC/EG with a 13 wt. % Pt loading where EG is the encapsulated graphitized carbon showed an increase in current density compared to Pt/C for EOR [30]. This is a clear indication that the presence of Si (2.3 wt.%) in Pt/p-OLCs played a role in the increase in current density. However, in this work, we continued with Pt/N-OLCs as they contained fewer impurities and N-OLCs were the most thermally stable.

6.4.6 Conclusions

Pt/p-OLCs, Pt/F-OLCs, and Pt/N-OLCs were successfully synthesized. The PXRD displayed the successful incorporation of Pt in the various OLCs materials, and this was corroborated by the XPS data. The Pt/p-OLCs displayed the presence of Si 2p which was absent in Pt/F-OLCs and Pt/N-OLCs. The XPS data also showed the successful doping of N-OLCs through the presence of organic N, cyanides, organic N, and azides. The D and G bands were observed from Raman spectroscopy, which was from the OLCs, and it was noted that after the incorporation of Pt; the D and G bands shifted towards higher frequencies indicating that the

Waste engine oil-derived OLCs showed a different behaviour compared to OLCs produced from clean grapeseed oil, olive oil and ghee oil used by Sikeyi *et al.*, Mongwe *et al.*, and Shaku *et al.*, [16], [17], [23], [31]. The Pt nanoparticles exhibited different shapes on the different OLCs with particle sizes of Pt/p-OLCs > Pt/N-OLCs > Pt/F-OLCs. Cyclic Voltammetry revealed that the Pt/F-OLCs had no oxidation peak present and thus no current density was observed. Despite the large agglomerates of Pt particles, Pt/p-OLCs oxidized ethanol much better than Pt/N-OLCs. This was attributed to the impurities present in p-OLCs. This requires further studies, to study the effect of individual impurities on the electro-oxidation of alcohols. Since N-OLCs remained our purest form of support with minimal impurities, further studies were done using Pt/N-OLCs.

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Chapter 7: In-situ synthesis of Pt/WS₂/N-OLCs composite as catalyst support for the oxidation of ethanol fuel cells

7.1 Introduction

In the pursuit of sustainable energy solutions, the progression of efficient catalysts for DEFCs remains a pivotal endeavour [1]. In this context, the creation and analysis of novel catalysts mark important achievements in advancing the boundaries of clean energy technologies [2]. In this chapter, the culmination of our efforts in the synthesis and evaluation of Pt/WS₂/N-OLCs as a novel electrocatalyst for ethanol direct fuel cells is presented. As previously mentioned, ethanol fuel cells have a plethora of advantages that offer an alternative to conventional energy sources, owing to ethanol's renewability, high energy density, and reduced toxicity [3]. However, the realization of their full potential relies upon the synthesis of electrocatalysts that can address key challenges such as the sluggish ethanol oxidation kinetics and the stability of the catalyst [4]. The incorporation of WS₂ nanostructures into Pt-based catalysts, supported by nitrogen-doped onion-like carbon (N-OLCs), displays a novel approach to enhancing catalytic activity and durability in direct ethanol fuel cells. The motivation behind the synthesis of Pt/WS₂/N-OLCs catalyst lies in leveraging the unique properties of each component in the composite. Platinum, prominent for its catalytic prowess serves as the primary active site for ethanol oxidation [5]. The integration of WS₂ introduces additional catalytic sites and synergistic interactions expected to improve the overall performance of the electrocatalyst [6]. The N-OLCs were used as a support matrix providing high surface area, thermal stability, and conductivity [7]. In this chapter, we present a comprehensive analysis of the synthesized Pt/WS₂/N-OLCs electrocatalyst, including its structural characterization and electrochemical performance under operating conditions.

7.2 Materials and methods

7.2.1 Chemicals

Platinum acetylacetonate ($\text{Pt}(\text{acac})_2$), ethylene glycol ($\text{CH}_2\text{OH})_2$, ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), potassium hydroxide (KOH), oleylamine (OLA), thiourea ($\text{CS}(\text{NH}_2)_2$), tungstic acid (H_2WO_4), hexane (C_6H_{14}), and Nafion solution (5 wt.%) were purchased from Merck South Africa. All chemicals were of analytical grade and were used without further purification. N-OLCs were synthesized in this work (Chapter 4).

7.2.2 Experimental procedure

a. Synthesis of $\text{WS}_2/\text{N-OLCs}$

As discussed in Chapter 4 and 6, N-OLCs were the purest form of carbon support in this study, despite a superior current density displayed by the p-OLCs. As such, N-OLCs were used in further studies. For the synthesis of the composite, 0.10 g of tungstic acid and 200 mg of N-OLCs were added into 10 mL of OLA and stirred for 30 minutes and further ultrasonicated for 30 minutes. In a separate vessel OLA (10 mL) and thiourea (0.12 g) were degassed while constantly stirring at 120 °C in a three-neck round-bottom flask for 20 minutes. The temperature gradually increased to 200 °C. Once reached, the amalgamation of tungstic acid and N-OLCs was added to the round bottom flask, and the temperature was then raised to 320 °C. The reaction was held at this temperature for 45 minutes to facilitate the growth of WS_2 nanostructures on N-OLCs. The reaction mixture was then cooled for 5 minutes, and ethanol was added to isolate the colloids. The $\text{WS}_2/\text{N-OLCs}$ nanostructures were collected via centrifugation and washed multiple times with ethanol/hexane (1:1) to remove excess OLA. The resulting black precipitate was dried at room temperature.

b. Synthesis of $\text{Pt}/\text{WS}_2/\text{N-OLCs}$

In a standard experiment setup, 100 mg of $\text{WS}_2/\text{N-OLCs}$ and $\text{Pt}(\text{acac})_2$ was dispersed in ethylene glycol to produce 5 wt. % Pt loading and stirred for 30 minutes. The $\text{Pt}/\text{WS}_2/\text{N-OLCs}$ solution was refluxed for 6 hours at approximately 197 °C. The resulting suspension was centrifuged and washed with deionized water. The nanocomposite was dried at 100 °C to obtain $\text{Pt}/\text{WS}_2/\text{N-OLCs}$ and characterized using various characterization techniques.

7.2.3 Characterization techniques

The synthesized electrocatalysts were characterized using XRD, Raman spectroscopy, XPS, TEM, SEM, and EDS (See instrument specifications in Chapter 4). The electrochemical characterization is specified in Chapter 6.

7.3 Results and Discussion

7.3.1 Powder X-ray Diffraction and Raman spectroscopy

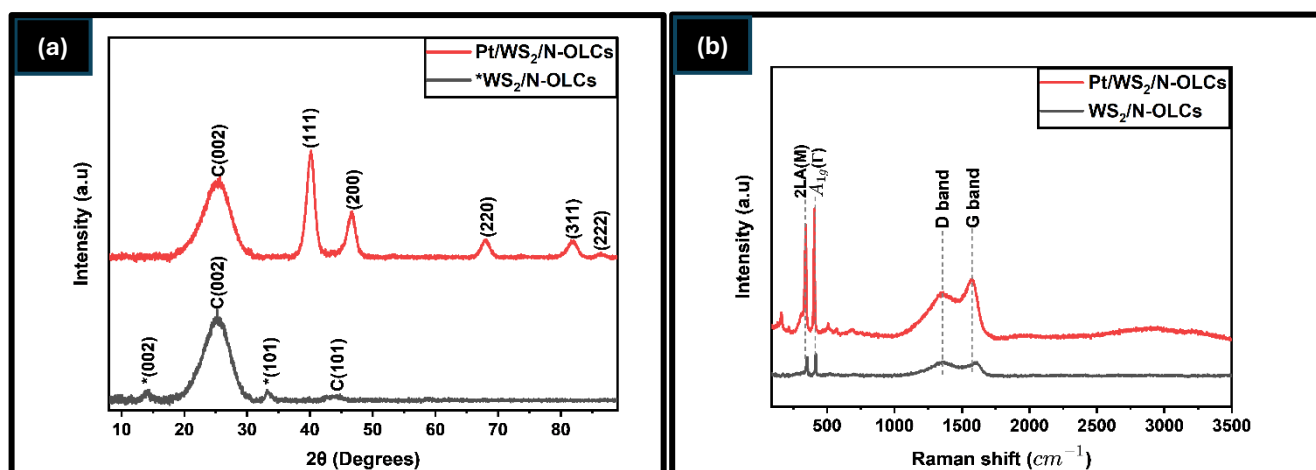


Figure 7.1: (a) PXRD pattern and (b) Raman spectra for the synthesized composites.

Figure 7.1 (a) displays the XRD patterns of the as-synthesized WS₂/N-OLCs, and Pt/WS₂/N-OLCs, respectively. The XRD peaks observed at $2\theta = 14.1, 25.2, 33.2,$ and 44.1 degrees for the WS₂/N-OLCs can be attributed to *(002), C(002), *(101), and C(101), where *(002) and *(101) belongs to the prominent peaks present in WS₂, and C(002) and C(101) belong to the prominent peaks present in N-OLCs [8]. The *(002) peak is attributed to the layered structure of WS₂, and it is observed that the N-OLCs peaks have shifted slightly from $2\theta = 25.30$ and 42.80 degrees to $2\theta = 25.22$ and 44.10 degrees due to the incorporation of WS₂ to the N-OLCs. It is noticeable that the diffraction peaks for the WS₂/N-OLCs composite are weaker than that of pure WS₂ and N-OLCs which demonstrates the low crystallinity of both WS₂ and N-OLCs [9]. The XRD peaks observed at $2\theta = 23.4, 40.2, 46.6, 68.0, 81.9,$ and 86.3 degrees for the Pt/WS₂/N-OLCs are assigned to C (002), Pt (111), Pt (200), Pt (220), Pt (311), and Pt (222) with a face centred cubic crystalline structure (PDF file PDF 01-087-0647) [10]. The XRD diffraction peaks *(002) and *(101) disappeared after the incorporation of Pt, and this could be

due to the amorphous nature of WS₂, and the diffraction peaks attributed to WS₂ in the WS₂/N-OLCs were weak. It is observed that the diffraction peaks assigned to Pt and N-OLCs have shifted after the addition of WS₂, and this could be attributed to the incorporation of WS₂. Gwebu *et al.*, observed that the diffraction peaks attributed to Pt and CNDs shifted to higher 2 θ values after incorporating TiO₂ into the Pt lattice which was found to reduce the platinum lattice parameter.

Raman spectroscopy (Figure 7.1(b)) were used to confirm the structure and chemical bonding of the synthesized WS₂/N-OLCs, and Pt/WS₂/N-OLCs composites. The Raman peaks for both WS₂ and N-OLCs were observed for both WS₂/N-OLCs and Pt/WS₂/N-OLCs composites. Both composites have two prominent active modes 2LA(M) and A_{1g}(Γ) which are attributed to the acoustic second-order longitudinal vibrational mode and out of-plane vibrational mode of sulphur atoms, respectively [11], [12]. The D and G bands are present due to the presence of N-OLCs in both composites. The Raman data complements the XRD data, confirming the physical interaction between WS₂ and N-OLCs in the composite. The 2LA(M) vibrational mode, A_{1g} vibrational mode, D band, and G band were found to be 351, 414, 1351, and 1602 cm⁻¹, respectively for the WS₂/N-OLCs. While for the Pt/WS₂/N-OLCs the 2LA(M) vibrational mode, A_{1g} vibrational mode, D band, and G band were found to be 340, 405, 1352, and 1571 cm⁻¹, respectively. Majumder *et al.*, and Zhang *et al.*, reported the Raman data for WS₂/C and WS₂/MWCNTs, respectively [9], [13] and found that the typical signals of WS₂ (351 and 417 cm⁻¹) and C (1356 and 1588 cm⁻¹) appeared on the Raman spectra which are compared to the results found in this study. Raman intensity of the G band was significantly higher than the D band. An increased intensity of the G band indicates a high degree of graphitization or crystallinity. The incorporation of Pt and WS₂ maintained the graphitic crystallinity of the N-OLCs, evidenced by the intense presence of the G band compared to the D band. The Raman data is observed in Table 7.1 and the Raman data for this work is comparable to what has been done in literature. The addition of Pt and WS₂ to the N-OLCs caused a red shift when compared to pure WS₂ and N-OLCs alone. This shift occurs due to the intermolecular van der Waals forces from the WS₂. These forces decrease interlayer interactions and cause structural disturbances on the onion rings of the N-OLCs, resulting in the observed red shift [13].

Table 7.1: Summary of Raman data.

Sample	2LA(M) (cm⁻¹)	A_{1g} (cm⁻¹)	D band (cm⁻¹)	G band (cm⁻¹)	Reference
WS₂	352	417	-	-	This work
N-OLCs	-	-	1357	1591	This work
WS₂/MWCNTs	352	417	1352	1591	[13]
WS₂/C	351	417	1356	1588	[9]
WS₂/N-OLCs	351	414	1351	1602	This work
Pt/N-OLCs	-	-	1351	1596	This work
Pt/ WS₂/N-OLCs	340	405	1352	1571	This work

7.3.2 Transmission electron microscopy

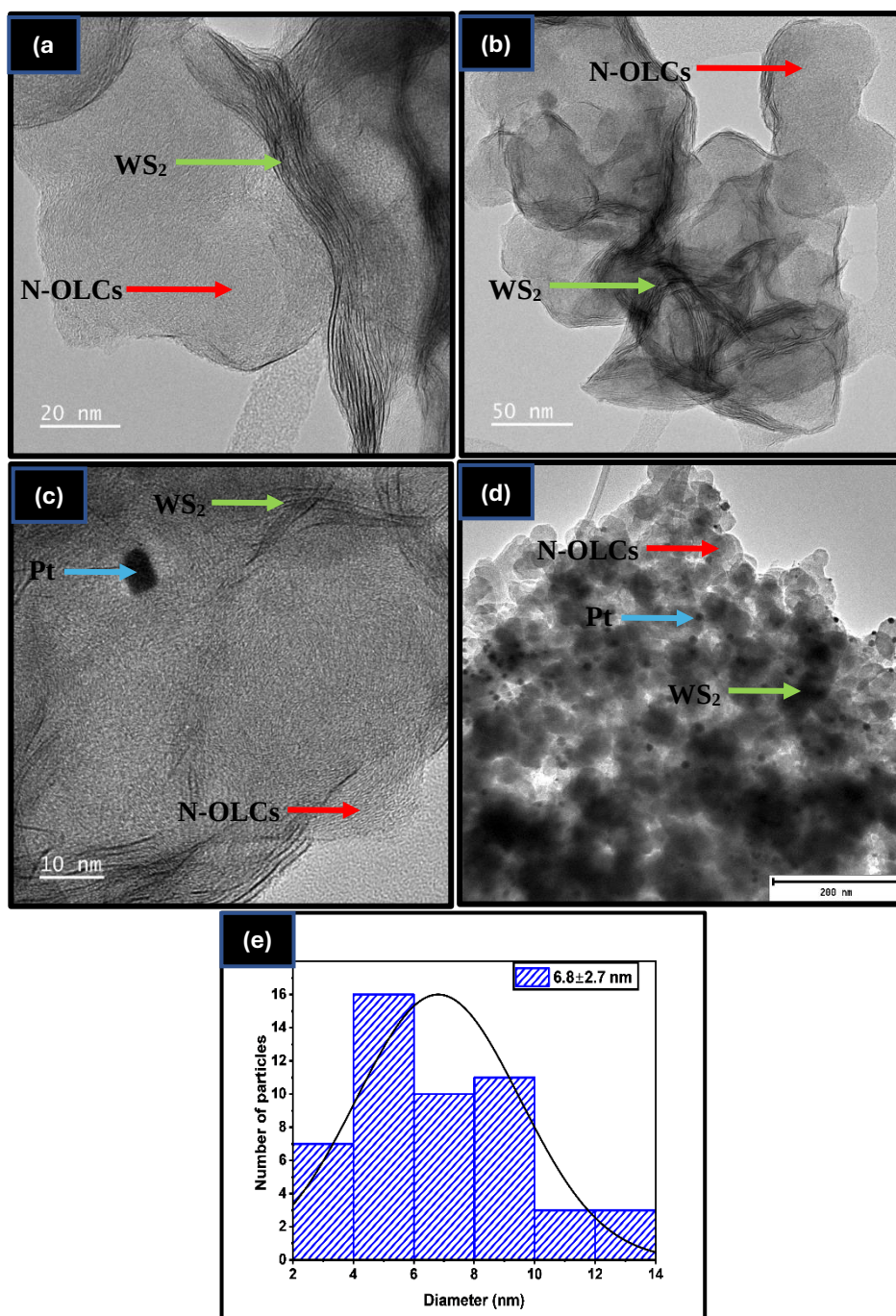


Figure 7.2: TEM images of (a) and (b) WS₂/N-OLCs, (c) and (d) Pt/WS₂/N-OLCs at different magnifications, (e) particle size distribution of Pt/WS₂/N-OLCs.

The morphology of the synthesized WS₂/N-OLCs, and Pt/WS₂/N-OLCs are displayed in Figure 7.2 (a) - (d). The WS₂ (shown by the green arrow) forms directly on top of the N-OLCs (shown by the red arrow) and encloses itself around the contour of the N-OLCs as observed in Figure

7.2 (a) and (b) for the WS₂/N-OLCs composite. The formation of the WS₂/N-OLCs resulted in the opening of the nanoflower like morphology of WS₂ allowing the WS₂ to interact with the N-OLCs. Zhang *et al.*, reported that WS₂ nanosheets resembling flowers wrapped around MWCNT vines through core shell growth for the application of lithium and sodium ion batteries [13]. Liu *et al.*, reported that Van der Waals forces and weak hydrogen bonds between WS₂ and SWCNT resulted in an excellent interaction between them [14]. It was also observed that carbon materials intercalate evenly between WS₂ layers [15]. Wang *et al.*, observed that the WS₂ nanosheets were sheathing on the conductive carbon in WS₂-NC and WS₂-C [16]. The addition of Pt to WS₂/N-OLCs resulted in the breakage of the WS₂ flower-like morphology as shown in Figure 7.2 (c) and (d). The reason for this phenomenon could be attributed to the reducing agent ethylene glycol. The flower-like WS₂ has a layered structure, and in this case, ethylene glycol could act as an exfoliating agent, reducing the layers of the flower-like WS₂, which results in the breakdown of its flower-like morphology. However, it does not appear to impact the interaction between WS₂ and N-OLCs, as we still observe WS₂ wrapping around the contour of N-OLCs. The Pt nanoparticles (shown by the blue arrow) are well distributed and appear to be interacting with the N-OLCs. Based on Figure 7.2 (d), it seems that the Pt/WS₂/N-OLCs possess a sandwich-like composition, resembling WS₂-Pt-N-OLCs as depicted in the schematic diagram (Figure 7.3). In this configuration, the Pt nanoparticles physically interact with both the WS₂ and N-OLCs, with Pt situated at the centre of the sandwich structure. When the composite was prepared ex-situ, no interaction was observed between WS₂ and N-OLCs (Figure S1). Figure 7.2 (e) shows the average particle size distribution of Pt on Pt/WS₂/N-OLCs which was found to be 6.8 ± 2.7 nm.

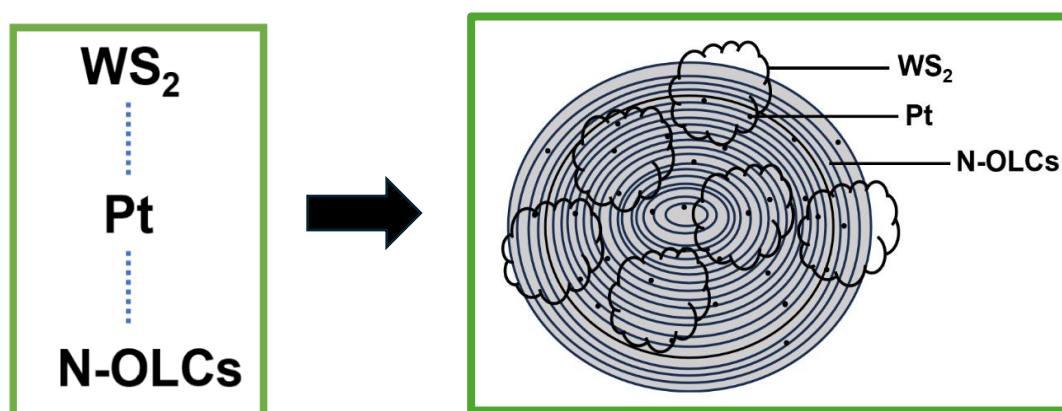


Figure 7.3: Schematic diagram of Pt/WS₂/N-OLCs sandwich like interaction.

7.3.3 Scanning electron microscopy

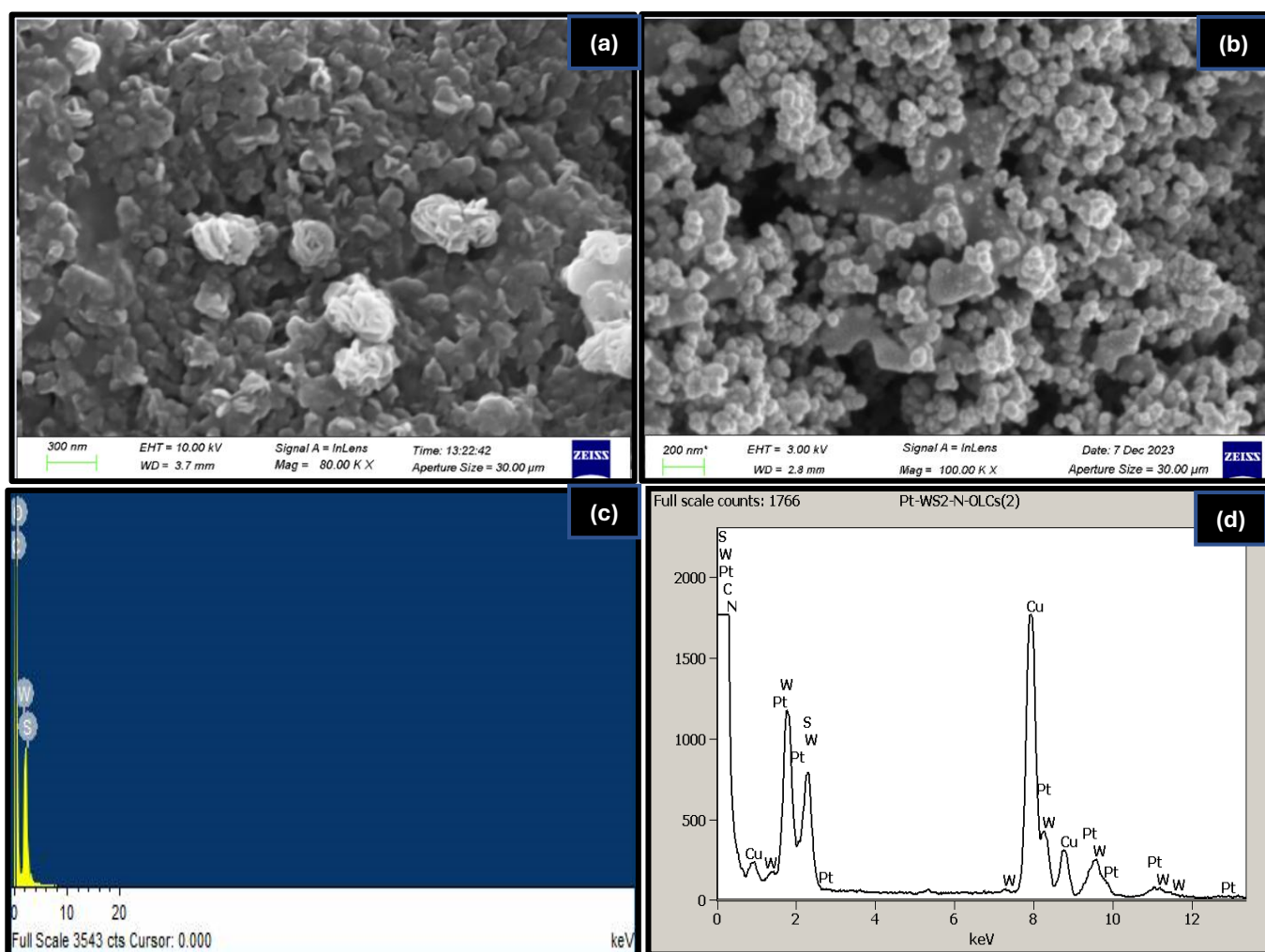
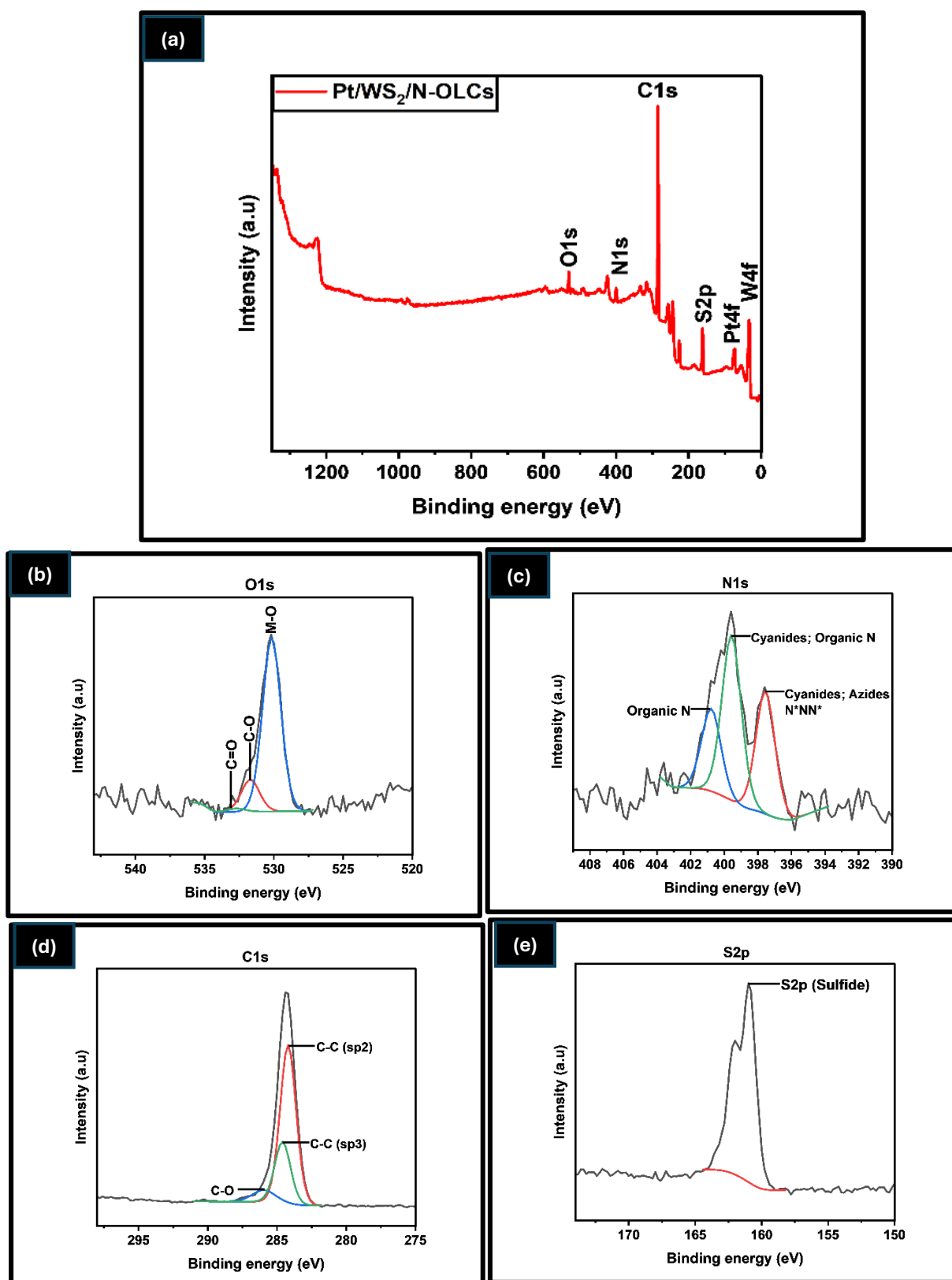


Figure 7.4: SEM images of (a) WS₂/N-OLCs, (b) Pt/WS₂/N-OLCs, (c) EDS spectrum of WS₂/N-OLCs, and (d) EDS spectrum of Pt/WS₂/N-OLCs.

SEM image of WS₂/N-OLCs is shown in Figure 7.4 (a) which displays the interconnected chain-like interaction of the N-OLCs which appear to be clustered. The WS₂ incorporated on the N-OLCs have a flower-like morphology and forms on top of the N-OLCs as observed on the SEM images in Figure 7.4 (a) and (b). Figure 7.4 (b) shows the Pt/WS₂/N-OLCs composite which displays the N-OLCs interconnected chained-like morphology, and it is also observed that during the incorporation of Pt, the flower-like morphology was disrupted due to the reducing agent thus causing defects in the morphology of WS₂. During the synthesis of Pt/WS₂/N-OLCs, it was observed that further oxidation of tungsten (W) occurred. This was confirmed by XPS analysis, which revealed the presence of both WO₂ and WO₃, whereas in

pure WS₂, only WO₃ was detected. Figure 7.4 (c) displays the EDS spectrum for WS₂/N-OLCs which confirms the synthesis of WS₂/N-OLCs. Figure 7.4(d) shows the EDS spectrum of Pt/WS₂/N-OLCs which confirms the incorporation of Pt and WS₂ on the surface of N-OLCs.

7.3.4 X-ray photon spectroscopy



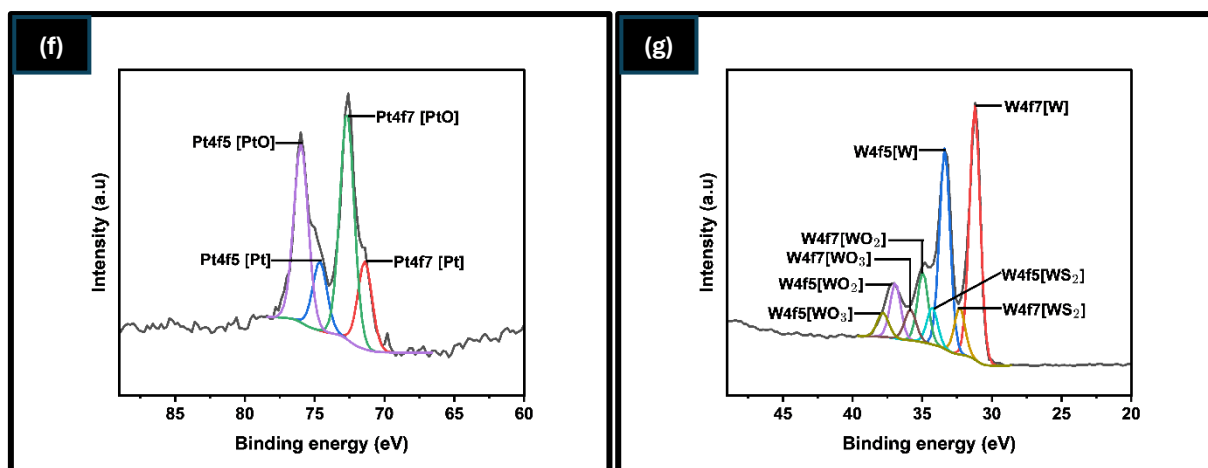


Figure 7.5: X-ray photon spectroscopy of the synthesized Pt/WS₂/N-OLCs composite. (a) Survey spectrum (b) - (g) High-resolution spectra.

The chemical phase and chemical composition of Pt/WS₂/N-OLCs were determined by XPS studies. The full survey spectrum of the Pt/WS₂/N-OLCs is shown in Figure 7.5 (a) along with the core levels present. The high-resolution XPS spectra focus on O 1s, N 1s, C 1s, S 2p, Pt 4f, and W 4f for the evaluation of the surface of Pt/WS₂/N-OLCs. The O 1s, N 1s, C 1s, S 2p, Pt 4f, and W 4f are observed at 530.8, 399.9, 284.8, 161.8, 73.3, and 32.9 eV, respectively. The deconvolution of the O 1s peak (Figure 7.5 (b)) showed the presence of oxygenated carbons C=O, C-O, and M-O where M represents a metal Pt or W. Figure 7.5 (c) showed the deconvolution of N 1s regional scan which indicates the presents of organic N, cyanides, and azides attributed to the N-OLCs. Figure 7.5 (d) illustrates the deconvolution of the C 1s regional scan, representing both WS₂ and N-OLCs within the composite, a feature also found in the pure materials. The C 1s peak exhibits three distinct peaks corresponding to C-O, C-C (sp²), and C-C (sp³). It is important to note that Pt/N-OLCs show the presence of O-C=O and C=O, which are absent in the C 1s peak for Pt/WS₂/N-OLCs, suggesting the disappearance of aromatic rings in the composite. Wang *et al.*, found the XPS peaks for WS₂-NC, the C 1s signal was located at 284.5, 285.5, 286.3, and 287.6 eV and they were assigned as follows C-C, C-N, C-OR, and C=O respectively [16]. From this composite, C was expected to be chemically bonded to N which was not observed in this study. This indicates that our composite has a purely physical interaction between WS₂/N-OLCs. Figure 7.5 (e) displays the deconvoluted S2p regional scan attributed to the presence of sulphur in WS₂. The S2p is due to the presence of sulphides in the composite. Figure 7.5 (f) shows the deconvoluted Pt 4f peaks for the Pt/WS₂/N-OLCs which

gave rise to the following peaks: a weak doublet Pt 4f5 and Pt 4f7 assigned to Pt and a medium doublet Pt 4f5 and Pt 4f7 attributed to PtO. This indicates the successful incorporation of Pt. Figure 7.5 (g) shows the deconvoluted W 4f regional scan which gave rise to the following peaks: a weak doublet W 4f5 and W 4f7 assigned to WO₃, a medium doublet W 4f5 and W 4f7 assigned to WO₂, a strong doublet W 4f5 and W 4f7 assigned to W, and a weak doublet W 4f5, and W 4f7 assigned to WS₂. In comparison to the synthesized WS₂, it is noted that Pt/WS₂/N-OLCs yield WO₂, indicating additional oxidation of tungsten during the composite synthesis process. Table 7.2 shows the summary of the atomic % composition, characterization, and assignments of the synthesized Pt/WS₂/N-OLCs material.

Table 7.2: Summary of the atomic composition and assignments from the fitting of the XPS spectra shown in Figure 7.2.

Element	Atomic %	Peak binding energy (eV)	Assignments
W	4.1	31.2	W
		32.3	WS ₂
		35	WO ₂
		35.8	WO ₃
Pt	0.9	71.4	Pt
		72.7	PtO
S	9	161.1	Sulfide
C	78.4	284.2	C-C (sp ²)
		284.6	C-C (sp ³)
		286	C-O
N	4.3	397.5	Cyanides; azides N*NN*
		399.6	Cyanides; organic N
		400.8	Organic N
O	3.3	530.2	Metal oxide
		531.7	C-O
		532.7	C=O

7.3.5 Cyclic voltammetry

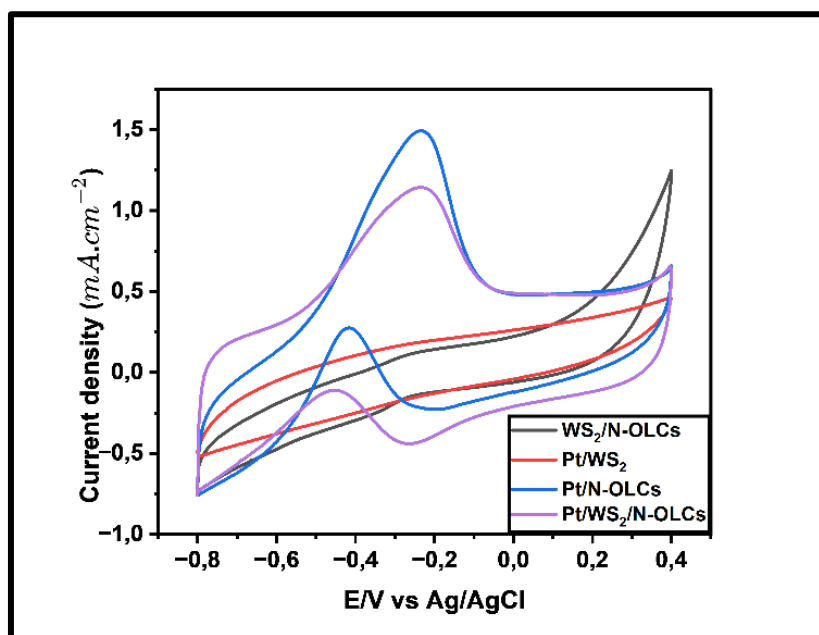


Figure 7.6: Cyclic voltammetry curves for WS₂/N-OLCs, Pt/WS₂, Pt/N-OLCs, and Pt/WS₂/N-OLCs in 1 M KOH + 1 M EtOH solution at a scan rate of 50 mVs⁻¹.

Figure 7.6 shows the cyclic voltammetry curves of ethanol electrooxidation on WS₂/N-OLCs, Pt/WS₂, Pt/N-OLCs, and Pt/WS₂/N-OLCs. The electrocatalytic response of WS₂/N-OLCs and Pt/WS₂/N-OLCs was determined by cyclic voltammetry shown in Figure 7.6. The Pt/WS₂ and WS₂/N-OLCs did not display any catalytic activity as there are no anodic and cathodic peaks present. This could be attributed to the inadequate adsorption/desorption of hydroxyl ions [17]. The anodic scan for the Pt/WS₂/N-OLCs electrocatalyst shown in Figure 7.6 displays a peak at -0.23V which is due to the adsorption/desorption of hydroxyl ions. The cathodic scan for Pt/WS₂/N-OLCs displays a wide peak at -0.27 V. This peak is a result of the reduction of Pt-O and was incorporated to determine the charge of the monolayer of the chemisorbed oxygen [17], [18], [19]. The anodic scan for Pt/N-OLCs displayed a peak at -0.23 V and a cathodic peak at -0.20 V. From the CV for Pt/WS₂/N-OLCs it is observed that at the cathodic scan, a peak appeared after the addition of WS₂ at -0.27 V. This indicates that the addition of WS₂ has the potential to improve the electro-oxidation of ethanol. The current density for Pt/WS₂/N-OLCs was found to be 1.2 mA/cm² which was slightly less than the current density for Pt/N-OLCs which was found to be 1.5 mA/cm² (chapter 6). The existence of the reverse peak

suggests that WS₂ functions as a co-catalyst rather than merely a support. WS₂/N-OLCs display no catalytic activity and the flower-like morphology of WS₂ was maintained as observed in the TEM and SEM images. This could be attributed to WS₂'s inability to cleave ethanol C-C bonds in the flower-like state [17]. It is interesting to note that when the flower-like morphology was disrupted during the incorporation of Pt; the Pt/WS₂/N-OLCs composite displayed catalytic activity. This could be attributed to the WS₂ nanoparticles further disturbing the structure of the N-OLCs. This behaviour indicates that morphological structure and electrocatalytic behaviour have a relation [20]. Ferreira *et al.* reported that MoS₂@MWNT exhibited superior performance compared to WS₂@MWNT for both ORR and OER. While both catalysts demonstrated electrocatalytic activity, the results indicated that further improvements are possible [20]. Gwebu *et al.* reported that fCNDs-WO₃ was not catalytically active towards methanol and ethanol oxidations due to the inability to adsorb/desorb hydroxyl ions but Pd/fCNDs-WO₃ showed improved catalytic performance due to the addition of WO₃ acting as a co-catalyst [17]. Pt/WS₂/N-OLCs is catalytically active with WS₂ and traces of WO₃ playing the role of co-catalysts but the current density observed leaves room for further enhancements. An excellent anode catalyst should have an increased current density in the forward scan and Pt/WS₂/N-OLCs have the potential to be an excellent anode catalyst.

Table 7.3: Comparison of the electrocatalytic performance from CV curves using current density.

Samples	Pt/Pd loading (wt. %)	Current Density (mA/cm²)	Reaction	References
Pt/p-OLCs	5	2.30	1 M KOH + 1 M EtOH	This work
Pt/F-OLCs	5	No catalytic activity	1 M KOH + 1 M EtOH	This work
Pt/N-OLCs	5	1.50	1 M KOH + 1 M EtOH	This work
WS ₂ /N-OLCs	-	No catalytic activity	1 M KOH + 1 M EtOH	This work
Pt/WS ₂ /N-OLCs	5	1.20	1 M KOH + 1 M EtOH	This work
Pd/ox-OLCs	10	14.5	1 M KOH + 1 M EtOH	[21]
Pd/N-OLCs	10	17.4	1 M KOH + 1 M EtOH	[21]
fCNDs-WO ₃	-	No catalytic activity	0.1 M KOH + 1 M EtOH	[17]
Pd/fCNDs-WO ₃	2.5	87.24	0.1 M KOH + 1 M EtOH	[17]
MoS ₂ @MWNT	-	0.73	ORR	[6]
WS ₂ @MWNT	-	0.70	ORR	[6]

In summary, the following deductions could be made from the study:

- (i) N-OLCs remain superior as electrocatalyst supports.
- (ii) WS₂, suppressed the performance of Pt-N-OLCs, contrary to this, N-OLCs significantly improved the electrocatalytic activity of WS₂.
- (iii) WS₂ and traces of WO₃ act as co-catalysts, rather than a support material.

7.3.6 Conclusions

WS₂/N-OLCs and Pt/WS₂/N-OLCs were successfully synthesized. The PXRD pattern indicated the successful incorporation of WS₂ onto N-OLCs to form WS₂/N-OLCs and the successful integration of Pt in Pt/WS₂/N-OLCs. WS₂ was not visible on the PXRD pattern for Pt/WS₂/N-OLCs due to its amorphous nature, but it was observed on TEM and SEM images. XPS further confirmed the formation of WS₂/N-OLCs and Pt/WS₂/N-OLCs. The Raman spectra revealed structural disturbances in the N-OLCs after the incorporation of both Pt and WS₂, evidenced by a red shift. However, both composites were confirmed by the presence of Raman peaks characteristic of WS₂ and N-OLCs. TEM and SEM images depicted the morphology of WS₂/N-OLCs and Pt/WS₂/N-OLCs, showcasing the quasi-spherical morphology of N-OLCs which remained interconnected after incorporating Pt and WS₂. During the synthesis of WS₂/N-OLCs, WS₂ nanostructures formed on the N-OLCs with a flower-like morphology. Integrating Pt into WS₂/N-OLCs destroyed the flower-like morphology of WS₂ due to the reducing agent ethylene glycol. WS₂/N-OLCs were found to be not catalytically active, while Pt/WS₂/N-OLCs exhibited catalytic activity towards the oxidation of ethanol. Pt/WS₂/N-OLCs demonstrated the potential to yield improved results, as observed from the obtained current density.

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Chapter 8: Conclusions and recommendations

8.1 Conclusions

The study aimed to synthesize Pt/WS₂/N-OLCs and develop Pt- based electrocatalysts for the electro-oxidation of ethanol in direct alcohol fuel cells. In this research project p-OLCs were successfully synthesized from waste engine oil using the flame pyrolysis method. The successful purification and functionalization of p-OLCs into F-OLCs, followed by doping with melamine to produce N-OLCs, was completed. Pt was subsequently dispersed on the synthesized OLCs. The synthesis of WS₂ was effectively achieved using the colloidal method and finally Pt/WS₂/N-OLCs were successfully synthesized.

8.1.1 Synthesis, doping and functionalization of onion-like carbons from waste engine oil

The synthesized F-OLCs, and N-OLCs displayed increased surface area due to the addition of functional groups and doping with nitrogen. The increase in surface area was confirmed by the BET surface area analysis and the average diameter which was obtained using TEM. N-OLCs were thermally stable without impurities. Flame pyrolysis still offers a cheap, sustainable route for the production of OLCs.

8.1.2 Synthesis of WS₂ using the colloidal method

WS₂ was successfully synthesized using the colloidal method and had a flower-like morphology confirmed by both TEM and SEM. The chemical composition and structure of WS₂ were determined using XRD and XPS which further revealed the presence of WO₃. The presence of the (002) validated that WS₂ was a layered structure which was substantiated by Raman data.

8.1.3 Synthesis of Pt supported on pristine, functionalized, nitrogen-doped OLCs for direct ethanol fuel cells.

Pt was successfully dispersed on p-OLCs, F-OLCs, and N-OLCs. PXRD showed the presence of Pt peaks and carbon which was further substantiated by XPS data. The doping of nitrogen was confirmed by XPS which displayed the existence of organic N, cyanides, and azides. It was observed from the TGA that the Pt-based OLCs showed structural disturbances of the OLCs after the incorporation of Pt. It was interesting to observe that waste engine oil behaved differently electrocatalytically from pure oils like grapeseed oil, olive oil, and ghee oil found in the literature. TEM showed the dispersion of Pt nanoparticles on p-OLCs, F-OLCs, and N-

OLCs which had different particle sizes and shapes. The EDS data corroborated the XPS data by displaying the presence of Pt for the Pt-based OLCs. Pt/p-OLCs displayed a higher current density from the cyclic voltammetry compared to Pt/N-OLCs. Pt/F-OLCs displayed no oxidation peak therefore no current density was determined.

8.1.4 WS₂/N-OLCs composite as catalyst support for the oxidation of ethanol fuel cells

WS₂/N-OLCs and Pt/WS₂/N-OLCs were successfully synthesized. WS₂ was successfully incorporated into N-OLCs which was substantiated by XRD. Pt was successfully integrated to form Pt/WS₂/N-OLCs. It was observed after the incorporation of Pt into WS₂/N-OLCs that the WS₂ nanoflowers disintegrated as a result of the reducing agent as observed in both the TEM and SEM images. The N-OLCs maintained the quasi-spherical and interconnected interaction after the addition of Pt and WS₂. WS₂/N-OLCs were found to be not catalytically active, while Pt/WS₂/N-OLCs exhibited catalytic activity towards the oxidation of ethanol. Pt/WS₂/N-OLCs showed the potential to yield improved results, as observed from the obtained current density. Pt/p-OLCs performed better than both Pt/N-OLCs and Pt/WS₂/N-OLCs.

8.2 Recommendations

- (i) **Optimization of the electrocatalysts:** Further optimization will be required for the electrocatalysts to improve the electrocatalytic activity towards ethanol oxidation. The percentage of WS₂ nanoflowers should be increased to optimize the WS₂ content in the composite.
- (ii) **Role of other co-catalysts:** The p-OLCs displayed superior alcohol oxidation compared to their counterparts, which was attributed to impurities. The effect of individual metal impurities contained in p-OLCs requires further studies.
- (iii) **Performance against the commercial Pt/C catalyst:** Although many studies have proved that with the developments of new technologies, the performance of the commercial Pt/C catalyst could be surpassed, it is recommended that electrocatalysts be compared with the commercial Pt/C.
- (iv) **Alternative synthesis route:** The microwave-assisted method could be explored to synthesize the Pt/WS₂/N-OLCs this could prevent the destruction of the WS₂ nanoflowers.

(v) **Different reducing agents:** Exploring an alternative reducing agent could be beneficial thus doing a study using different reducing agents and determining which one does not break the WS₂ flowers could improve the electrocatalyst. Gwebu *et al.*, used a sonochemical-assisted borohydride reduction method to deposit Pd nanoparticles to synthesize Pd/fCNDs-WO₃ composite and observed that the catalyst had improved performance towards methanol and ethanol electrooxidation [1]. Varying the ratios of the EtOH and KOH electrolytes could improve the electrocatalytic activity of the Pt/WS₂/N-OLCs. Changing the base (KOH) electrolyte to an acid electrolyte like H₂SO₃ and comparing how the catalyst performs in both acidic and basic media. Further electrochemical studies need to be performed to determine the stability of the electrocatalyst using chronoamperometry and testing the electron transfer resistance using impedance spectroscopy.

Appendix: Supplementary data

Chapter 4

Equation 4.1 shows the calculation used to obtain the percentage yield of the synthesized OLCs.

$$\begin{aligned}\% \text{ conversion} &= \frac{\text{mass of p-OLCs (g)}}{\text{mass of waste engine oil (g)}} \times 100 \quad \dots \text{Equation 4.1} \\ &= \frac{6.5648 \text{ g}}{189.194 \text{ g}} \times 100 \\ &= 3.47\%\end{aligned}$$

$\therefore$ % yield is approximately 3.47%

The interlayer spacing was calculated as follows:

$$d_{(hkl)} = \frac{n\lambda}{2\sin\theta} \quad \dots \text{Equation 4.2}$$

Where $d_{(hkl)}$ = Interplanar spacing (d-spacing)

n = order of reflection

λ = X-ray wavelength

θ = angle of incidence

Sample calculation: Interplanar spacing for p-OLCs.

$$2\theta = 25.3$$

$$\theta = 12.65$$

$$d_{(002)} = \frac{(1)(0.154184 \text{ nm})}{2\sin(12.65)}$$

$$d_{(002)} = 0.35 \text{ nm}$$

Chapter 6

6.4.2 XPS

Table S1: Summary of the atomic composition and assignments from the fitting for the Pt/p-OLCs XPS spectra shown in Figure 6.3

Element	Atomic %	Peak binding energy (eV)	Assignments
Pt	0.4	71.3	Pt
		72.6	PtO
Si	2.1	101.9	Organic Si
C	89.4	284.5	C-C
		285.8	C-O
		287.1	C=O
O	8	530.3	Metal oxide
		531.9	C-O
		533.3	C=O

Table S2: Summary of the atomic composition and assignments from the fitting for the Pt/F-OLCs XPS spectra shown in Figure 6.3

Element	Atomic %	Peak binding energy (eV)	Assignments
Pt	0.7	71	Pt
		72.4	PtO
C	78.8	284.1	C-C (sp ²)
		285	C-C (sp ³)
		286.2	C-O
		287.5	C=O
		288.7	O-C=O
N	1.7	399.7	Cyanides; Organic N
O		530.5	Metal oxide

	18.7	531.5	C-O
		532.9	C=O

Table S3: Summary of the atomic composition and assignments from the fitting for the Pt/N-OLCs XPS spectra shown in Figure 6.3

Element	Atomic %	Peak binding energy (eV)	Assignments
Pt	1.4	71.1	Pt
		72.6	PtO
C	80.8	284.2	C-C (sp ²)
		284.6	C-C (sp ³)
		285.8	C-O
		287.7	C=O
		289.5	O-C=O
N	12.8	398.2	Cyanides; Azides N*NN*
		399.9	Cyanides; Organic N
		400.1	Organic N
O	5	530.4	Metal oxide
		531.7	C-O
		532.9	C=O

Chapter 7

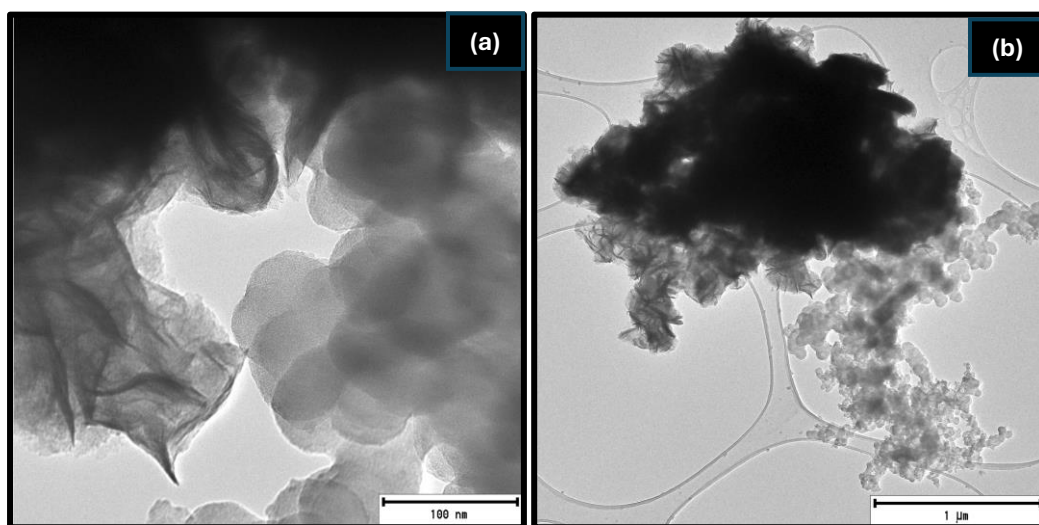


Figure S1: TEM image of WS₂/N-OLCs composite using an ex-situ method