

**Colloidal synthesis of NbSe₂
nanoflowers and Nb₂Se₉ nanorods for
application as counter electrode
materials in dye sensitized solar cells**



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Master of Science

By

Tshwarela Kolokoto

670850

A black ink signature of Tshwarela Kolokoto.

20/02/2019

Candidate

(Tshwarela Kolokoto)

Date

A red ink signature of Prof N. Moloto.

20/02/2019

Supervisor

(Prof N. Moloto)

Date

Declaration

I declare that the work reported herein is my own independent work, submitted at the School of Chemistry, University of the Witwatersrand, Johannesburg. This work has not been submitted for any degree or examination in any other institution of higher learning.



Candidate
(Tshwarela Kolokoto)

20/09/2019

Date

Abstract

Solar cells are amongst the most promising technologies for alternative electricity generation due to the abundance of the sun and their reduced impact on the environment. Among many solar cell designs, dye-sensitised solar cells (DSSCs) have the potential to be used at large scale however they have some disadvantages such as low power conversion efficiency (PCE), poor stability and high cost. As such, researchers have investigated various ways of improving on these disadvantages. In this study, we considered the use of niobium selenide nanoparticles as counter-electrodes (CEs) to replace Pt-CEs in DSSCs with the attempt to lower the cost of the device. Pt is an expensive noble metal with high electrocatalytic activity and stability, so a replacement electrode should be lower in cost while maintaining the high electrocatalytic activity and stability. Niobium selenide nanoparticles were of interest due to their unique and tunable properties such as catalytic, electronic, optical and magnetic. NbSe₂ is a 2D-layered material and Nb₂Se₉ is a 1D material made up of chains, each layer or chain is held together by weak van der Waals forces. Therefore, to solve these problems, two important factors needed to be evaluated; the synthetic route of the nanoparticles and the fabrication of the CE.

Colloidal synthesis method was used due to its flexibility, allowance for reaction parameter variation and use of low temperatures and reaction times. As such, the following reaction parameters were varied: reaction time, temperature, precursor concentration, capping agent, as well as Nb and Se precursors to investigate the optimum conditions for the synthesis of NbSe₂ and Nb₂Se₉ nanoparticles. NbSe₂ nanoflowers were favoured at 320 °C for 120 min in oleylamine (OLA) at a concentration of 0.125 M where NbCl₅ was the metal precursor used. The use of selenourea (SU) as a selenium precursor, with the rest of the reaction parameters unchanged, produced rhombohedral NbSe₂ nanoflowers while Se and SeO₂ produced hexagonal NbSe₂ nanoflowers. On the other hand, Nb₂Se₉ nanorods were formed when the temperature was decreased to 280 °C and the concentration was increased to 0.500 M, hexadecylamine (HDA) or 1-octadecene (ODE), and NbF₅ as a metal precursor were used. The use of Se produced monodispersed and crystalline Nb₂Se₉ triclinic phase nanorods than SU and SeO₂. This is a clear indication that each reaction parameter has an effect on the nucleation and growth process of the nanoparticles and in turn on their properties. OLA, HDA and ODE were capping the surface of the nanoparticles. However from both FTIR and NMR spectroscopies evidence of oxidation of the capping agents was observed.

The electrocatalytic activity of NbSe₂ nanoflowers and Nb₂Se₉ nanorods were investigated and compared with that of Pt using cyclic voltammetry. Two methods were used to fabricate the CEs i.e. spin-coating and drop-casting method. The spin-casted CEs were more stable and reproducible compared to the drop-casted CEs. Moreover, Nb₂Se₉ CEs were not stable irrespective of the method of fabrication used. The spin-coated NbSe₂ CE had a higher current density and electrochemical double layer capacitance than both Pt and spin-coated Nb₂Se₉ CEs. This was an indication that NbSe₂ nanoflowers have a higher electrocatalytic activity than Pt (because NbSe₂ had a current density of 5.88 mA/cm² whereas Pt was 4.86 mA/cm²) due to high surface area and coverage. As such, it has the potential to produce cost-effective DSSCs by replacing Pt.

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Dedication

I dedicate this to my mother, my family and my future.

Presentations

- Oral presentation at Catalysis Organometallics and materials' (CATOMAT) seminar held at Chemistry department, University of the Witwatersrand on the 04/05/2017
- Poster presentation at the 7th Annual Gauteng Nanosciences Young Researchers' Symposium (2017 SANi-NYRS) on the 20/10/2017. (Best poster 3rd place)
- Poster presentation at the 8th cross-faculty postgraduate symposium (WITS) 25/10/2017 and 26/10/2017. (Best poster 3rd place)
- Oral presentation at Catalysis Organometallics and materials' (CATOMAT) seminar held at Chemistry department, University of the Witwatersrand on the 23/03/2018
- Poster presentation at the 7th international conference on nanoscience and nanotechnology (NanoAfrica 2018) from the 22/04/2018 to the 24/04/2018. (Best poster 3rd place)

List of Publications

- Phase and shape control of niobium selenide nanostructures by varying reaction parameters, to be submitted to *2D Materials* (2019).
- NbSe₂ and Nb₂Se₉ as alternative electrode materials, to be submitted to *Materials Research Bulletin* (2019).

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List of symbols and abbreviations

CB	- Conduction band
CE	- Counter-electrode
DSSC	- Dye-sensitised solar cell
EDX	- Energy-dispersive X-ray spectroscopy
E_g	- Energy gap
FTO	- Fluorine doped tin oxide
HDA	- Hexadecylamine
HOMO	- Highest occupied molecular orbital
HRTEM	- High-resolution transmission electron microscopy
ITO	- Indium-doped tin oxide
LUMO	- Lowest unoccupied molecular orbital
NP	- Nanoparticle
ODE	- 1-Octadecene
OLA	- Oleylamine
PCE	- Photoelectric conversion efficiency
SCAC	- Stacked single-chain atomic crystals
SEM	- Scanning electron microscopy
TCO	- Transparent conductive oxide
TEM	- Transmission electron microscope
TMC	- Transition metal chalcogenide
TMDC	- Transition metal dichalcogenide
TOP	- Trioctylphosphine
UV-Vis	- Ultraviolet-visible spectrophotometry
VB	- Valence band
XRD	- X-ray diffraction
XPS	-X-ray photoelectron spectroscopy

Synopsis

The aim of the study was to synthesize 2D layered niobium selenide nanostructures (NbSe_2 and Nb_2Se_9) using the colloidal method and evaluate their electrocatalytic properties using cyclic voltammetry for potential application as counter electrodes in dye-sensitized solar cells in order to replace the expensive Pt counter electrode. The layout of the dissertation is therefore shown below:

Chapter 1: is comprised of the general background, motivation and rationale for the study as well as aims and objectives.

Chapter 2: is the literature review of metal chalcogenide, their properties and synthetic routes. In addition, a short review on DSSCs in particular the types and properties of counter electrodes and the use of metal chalcogenides as counter electrodes.

Chapter 3: reports on the phase and shape control of niobium selenide nanostructures through variation of reaction parameters.

Chapter 4: reports on the effect of the selenium precursor on the properties of NbSe_2 .

Chapter 5: reports on the synthesis Nb_2Se_9 using Se, SeO_2 and selenourea as selenium precursors.

Chapter 6: reports on the investigation of NbSe_2 and Nb_2Se_9 as alternative electrodes for DSSCs.

Chapter 7: critically looks at the conclusions and suggests possible future studies.

Chapter 1

General background

1.1 Introduction

In the world that we live in today, electricity is very essential. As such, it is known that it affects the country's economy and social development [1]. Africa derives most of its energy from burning biomass (wood and animal waste) and fossil fuels (gas, oil, and coal). South Africa generates the majority of its electricity from coal and in 2012 this was approximated to be 69 % as shown in **Figure 1.1** [2]. Although coal is able to provide electricity that meets the entire country's demand it has many negative environmental and health impacts such as coal combustion waste, coal mine waste (acid mine drainage), toxic land fires and toxic coal fires. With the continuously increasing demand for electricity and the ever increasing prices of electricity, Eskom, South Africa's major electricity provider, had to resort to unfavourable solutions to curb the demand and burden on the electric grid such as load shedding to cut down on the electricity usage to prevent a total blackout [3]. Thus alternative cost-effective, sustainable and clean electricity sources are needed. The biggest challenge is to use cleaner energy supplies that will generate electricity that will meet the current demand while maintaining low electricity prices to reduce the negative social, environmental and economic effects [2].

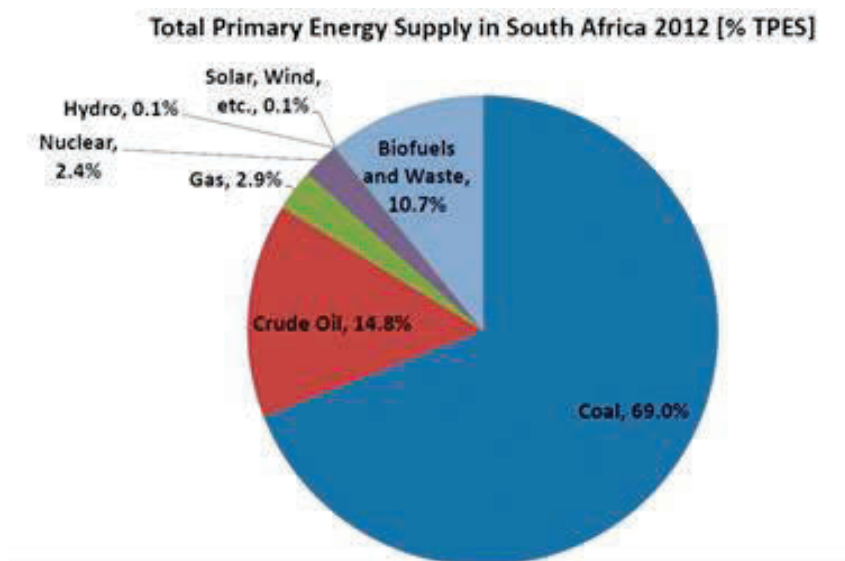


Figure 1.1: Indication of the various energy sources used in South Africa in 2012 [2].

Renewable energy refers to sources such as solar, wind, hydro and geothermal. These energy sources are naturally replenished and, will not be exhausted throughout the human lifetime, unlike fossil fuels, referred to as finite resources, which are effectively limited [2]. Renewable sources can assist in diversifying energy carriers, minimize the use of fossil fuels, pollution and lower the dependency on imported fossil fuels [2]. However, renewable sources need to be used along with economically feasible technologies. Much of research has gone into potentially using renewable energy to generate electricity in the production of solar cells.

Solar cells are devices that convert solar radiation into electrical energy [4-6]. They are classified into III generations (1st, 2nd, and 3rd) [7]. The 1st generation is based on single-crystalline Si solar cells, they have the highest power conversion efficiency and market footprint in the commercial industry. However, producing these solar cells is expensive hence they have very little impact on the energy market. The 2nd generation solar cells are based on the thin film processing technology and are made up of materials such as amorphous-Si, CdTe and CuInGaSe₂. Although they use cheaper processing technologies than the 1st generation solar cells, their low efficiencies have resulted in the overall costs of the panels to be as expensive. The 3rd generation solar cells are based on thin film processing technologies and use of novel materials and are currently under intensive research. Such solar cells already exist albeit at lab scale, and are among others, inorganic nanocrystal solar cells, organic solar cells and dye-sensitised solar cells (DSSCs) [7]. 3rd Generation solar cells, due to the novel properties of the materials and cheap processing technology are poised to surpass Si solar cells while still maintaining very low prices.

1.2 Problem statement

Electricity demand is continuously increasing and the sources used currently are not abundant. In addition, burning of biomass and fossil fuels (coal) has a negative impact on the environment. Moreover, the cost of electricity currently is quite high and continues to increase annually. Solar cells are available commercially but they are expensive and have low efficiencies. In order for us to be able to make them affordable, there are limitations that have been set by economics that the method in which the solar cell device is formed on a large-scale should be 10 times less than its commercial price [8]. That is the entire procedure required to make these devices should be relatively cheap so that the commercial price can be low. For alternative sources, solar is the most abundant and most reliable source of renewable energy and is therefore the most viable option and invariably so are solar cells.

DSSCs have shown promise as solar cells to compete in the energy market due to their simple design and use of cheap processing technologies. However, the choices of materials used such as the use of Pt as the counter electrode (CE) material as well as the low efficiencies become the biggest barrier in moving towards large scale production and commercialization [9].

1.3 Rationale

The DSSC market has been predicted to be over \$130 million in the year 2023; this is when used in portable and disposable electronics only [10]. Extending the use from portable and disposable to large panels for electricity generation will obviously increase its market share. The fact that this solar cell has many components adds to its advantages because there is room for improvement of each component to lower the costs with the use of cheaper alternatives and increase the efficiency [10, 11]. For examples, DSSCs use a TCO layer with high transparency and low resistance as compared to the expensive ITO or FTO coated glass substrate [12]. Herein, we propose the use of 2D layered niobium selenide as an alternative material for use as a counter electrode in order to eliminate the use of Pt. The aim is to lower the cost while not compromising the catalytic efficiency of the electrode. To further lower the cost, herein, we propose the use of a much cheaper synthetic method for niobium selenide. Niobium selenide is a layered material in bulk and to achieve 2D layered material, methods such as exfoliation, MBE as well as CVD have been widely used [13]. These methods use expensive equipment, are energy intensive and have low yields. Herein, we propose the use of a scalable colloidal method that uses mild conditions and cheap chemistry apparatuses [14].

1.4 Aims and objectives

The aim was to explore and understand the colloidal synthetic route of NbSe₂ nanoflowers and Nb₂Se₉ nanorods by investigating the effect of the reaction parameters as well as selenium precursors. Then finally, investigate the electrochemical properties of these nanomaterials for application as CEs in DSSCs using cyclic voltammetry.

As such, the following objectives were identified:

- Obtain the optimum reaction conditions for the synthesis of NbSe₂ nanoflowers and Nb₂Se₉ nanorods by varying the temperature, reaction time, concentration and capping agent.

- Investigate the effect of Se precursors on the NbSe₂ nanoflowers and Nb₂Se₉ nanorods synthesis.
- Investigate the electrochemical properties of the nanomaterials and their potential to substitute Pt-CEs.

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Chapter 2

Literature review

2.1 Transition metal chalcogenides

Transition metal chalcogenide (TMC) nanoparticles (NPs) are of interest due to their novel optical, electronic, catalytic and magnetic properties [1]. These properties are different from the bulk counterparts [2]. These NPs have at least one dimension in the range of 1-100 nm [3-6]. Their unique characteristics such as size (too small to be equivalent to the wavelength of an electron) can be explained by the quantum confinement theory of charge carriers, surface effects and geometrical confinement [2]. The bulk of the material is characterised by its band structure which can either be direct or indirect as well as the band gap (E_g) energy. The E_g is the minimum energy required to excite an electron from the valence energy band (VB) into the conduction energy band (CB). Basically, the NPs experience an elementary excitation due to absorption of a photon as such experience quantum confinement resulting in a finite motion along a confinement axis that is either 1D (quantum wires e.g. nanorods) or 2D (quantum wells e.g. nanosheets) [7, 8-11]. Strong quantum confinement results in quantised levels which are very different from the continuous band of the bulk [12-14], shown in **Figure 2.1**. Quantum confinement manifest when at least one of the dimensions of the NP is smaller than the Bohr exciton radius of the material, which will result in a modification of the band structure such that the charge carriers become spatially confined which subsequently blue shifts to higher energy [14-20]. It is this size regime that reveals the size-dependence of the band structure [20]. Therefore, the electron and holes density for both 1D and 2D quantum confined NPs can be expressed as;

$$\rho(E) \propto E^{\frac{d}{2}-1} \quad \text{where } d = 1, 2 \dots \quad (2.1)$$

where d is the number of dimensions and E is the energy measure from the bottom of the CB and from the top of the VB for electron and holes, respectively [7]. However, the density of states are no longer continuous and the number of discrete energy level appear due to quantum confinement effect since $d = 1$ and $d = 2$ for 1D and 2D NPs. This can be expressed as;

$$E_n = \left(\frac{\pi^2 \hbar^2}{2m_{e,h} l^2} \right) n^2 \quad \text{where } n = 1, 2 \dots \quad (2.2)$$

where l is the size along the confinement direction. Therefore, electronic and optical properties of NPs depend on the size of the NPs as a result of possible manipulation of the size of the exciton [7].

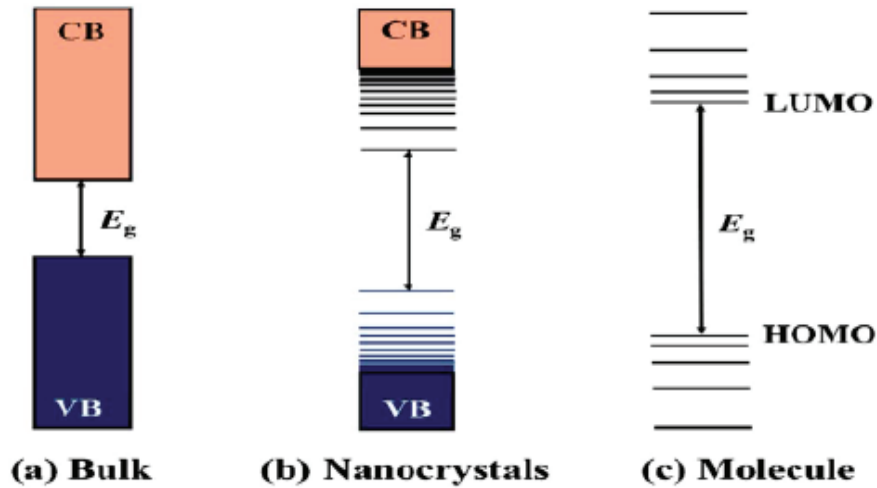


Figure 2.1: An illustration of the electronic energy levels [20].

2.1.1 Quantum confinement effects

In terms of optical properties, the quantum confinement effects can also be determined by the absorption spectra of the NPs, where a decrease in size will result in a blue-shift of the absorption peak to higher energy as shown in **Figure 2.2 (a)** [21]. The absorption peak is also known as an excitonic peak, which represents the amount of energy required to separate an electron and a hole. Furthermore, more than one absorption peak can be obtained that will be corresponding to optical transitions between the electronic energy levels of the NPs. Therefore, the position of the excitonic peak is dependent on the size of the NPs and the shape of the peak depends on the size distribution, morphology, and stoichiometry of the NPs. For instance, if the NPs are polydispersed then there will be a shoulder-peak in the absorption spectra [22]. NPs can be characterised by an E_g ranging between 0 and 4 eV and a band structure that is either direct or indirect. For the direct E_g the top of the VB and the bottom of the CB are found at the same k -value, whereas with an indirect E_g they are located at different k -values as shown in **Figure 2.2 (b)** [12, 15, 23].

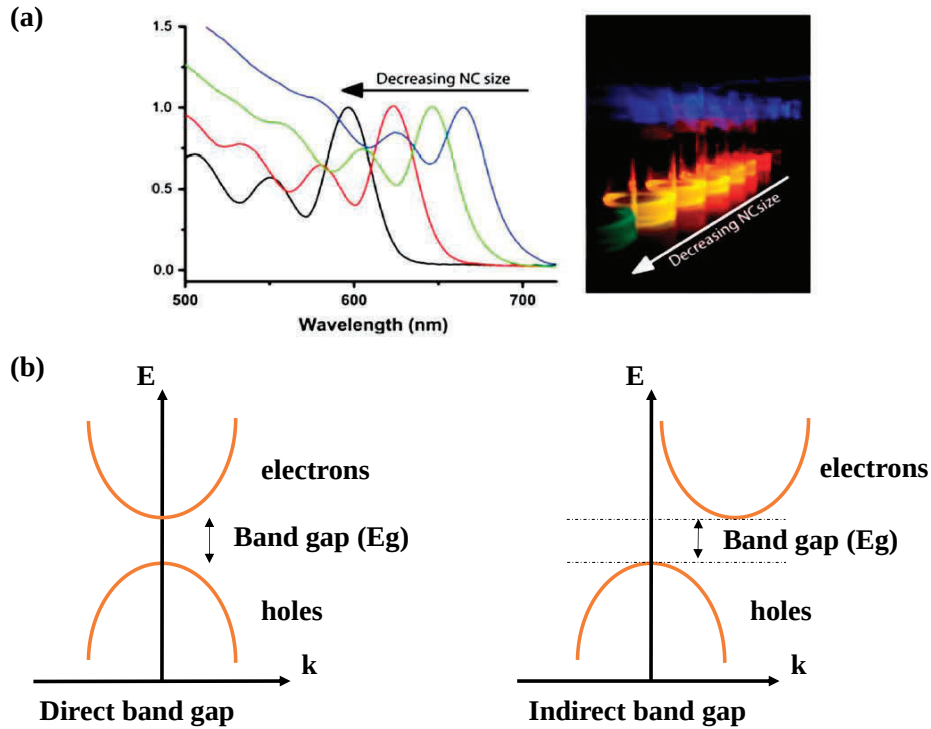


Figure 2.2: Schematic depiction of the quantum confinement effect: (a) (on the left) absorption spectra of colloidal suspensions of CdTe quantum dots with different sizes and (on the right) a picture of vials containing the colloidal suspensions of CdTe quantum dots under UV radiation [24, 25].

As such, the E_g is inversely proportional to the NP size with the emergence of discrete energy levels at the band-edges of both the VB and CB showed in **Figure 2.3** [23]. The $1S_h$ to $1S_e$ energy levels represent the lowest energy optical transition, whereas the $1P_h$ to $1P_e$ energy levels represent the second level transition. A strong confinement results in a large shift of the energy levels when the radius of the NPs is smaller than the excitonic Bohr radius. However, the opposite applies with weak confinement when the radius of the NPs is 2-3 times larger than the Bohr radius [23].

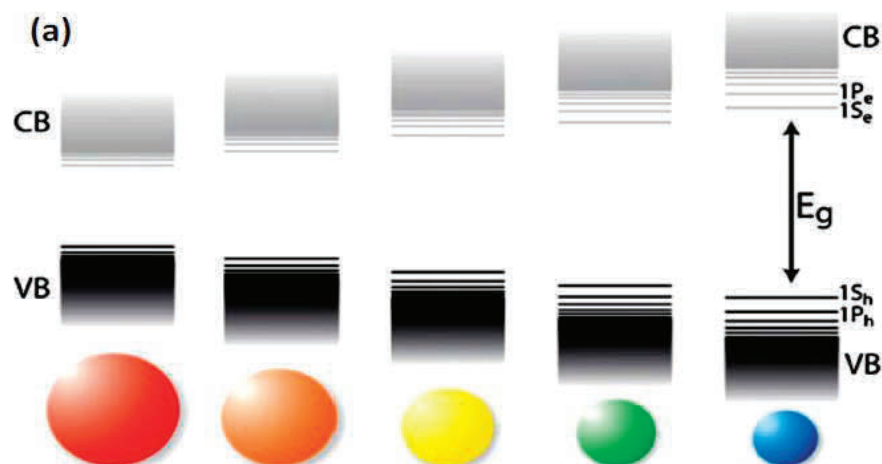


Figure 2.3: An illustration of quantum confinement effects showing the emergence of discrete energy level when the NP size decreases the E_g increases [23].

Metal selenides have been the most studied nanomaterials, due to their usage in major applications such as solar cells, biomedical diagnosis devices, sensors and light emitting diodes [26], specifically Nb_2Se_9 and NbSe_2 NPs which are low dimensional materials (1D and 2D, respectively) [27, 28]. Both structures have dangling bonds on their chains or sheets; therefore they have excellent optoelectronic properties [29]. 1D materials have been of interest due to their unique properties such as high carrier mobility, high chemical stability, high mechanical strength and high surface area [30-34]. The 2D materials on the other hand have unusual properties that are directly related to their structure. These materials have opened up new directions to research and have been used in various advanced applications [27].

2.1.2 NbSe_2 properties

Most transition metal dichalcogenides (TMDCs) of the transition metal in groups IV, V and VI belong to the well-known family of layered structures [35, 36]. Some of these 2D materials have been made by isolating the unit atomic layers from the bulk-layered structures [27, 28]. NbSe_2 has a crystal structure containing polymeric layers with the Nb-layer sandwiched between two Se-layers (i.e. Se-Nb-Se) and there is covalent bonding between Nb atom and Se atoms with each polymeric layer is held together by weak van de Waals interactions shown in **Figure 2.4** [35, 36]. The layers are closely packed and the arrangement of up to 6 layered structures has been reported.

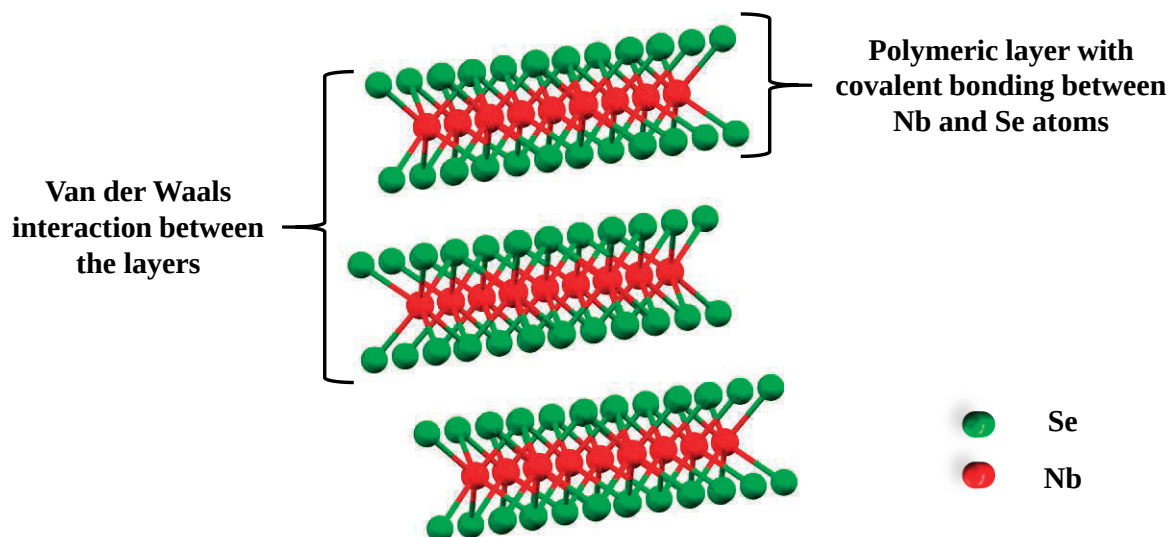


Figure 2.4: Detailed crystal structure of NbSe₂.

Most of the binding energy of the crystal is said to be concentrated within the layers, therefore there is very little energy difference between the stacking arrangements [36]. The weak van der Waals forces are responsible for the easy sliding of the layers relative to one another, thus providing a favourable matrix for intercalation reactions [35]. The coordination around the Nb atom can either be a distorted octahedral or trigonal prismatic [36]. They have shown potential to be used in various applications including microelectronic and optoelectronics as well as used as solar cell elements, lithium batteries, catalysis, and nanotribology and in other areas [35]. Since NbSe₂ has a layered structure, it is known to crystallise in the form of microplates [35]. Brixner *et al.* reported a two-layer structure of C7 (MoS₂) type [36]. This structure has a hexagonal phase (2H-NbSe₂) (**Figure 2.5 (a)**) with cell dimensions of $a = 3.45 \text{ \AA}$ and $c = 12.54 \text{ \AA}$. The coordination around the cation is trigonal prismatic and all the cations are aligned in the c -direction. They further reported a three-layer rhombohedral phased structure (3R-NbSe₂) (**Figure 2.5 (b)**) also of the MoS₂ type. Based on the hexagonal lattice the cell dimensions are $a = 3.45 \text{ \AA}$ and $c = 18.88 \text{ \AA}$. However, the cations in this structure are not aligned along the c -axis instead the excess metal atoms are located in the octahedral holes between the layers [36]. The hexagonal structure is the more favoured energetically stable structure [37].

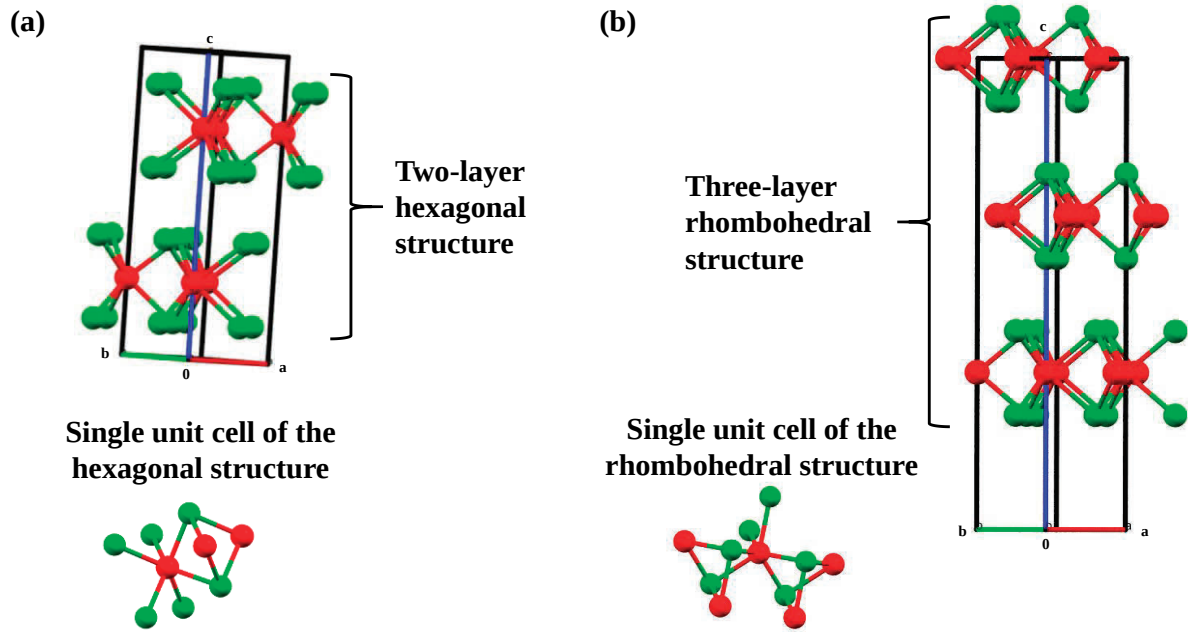


Figure 2.5: Crystal structure of (a) 2H-NbSe₂ and (b) 3R-NbSe₂ phase.

The electronic properties of NbSe₂ are shown in **Figure 2.6** below, which shows the band structure of NbSe₂ [37]. It is already known that NbSe₂ is metallic (because of the free electron in the CB) and because of the occurrence of the gap at around 1.5 eV above the Fermi level, this is an indication that NbSe₂ can be doped with a donor impurity to make an n-type semiconductor [37]. Since NbSe₂ has a similar structure to MoS₂, then the band structure of MoS₂ can be used to explain the band structure of NbSe₂ in more detail. There is an indirect to a direct E_g transition from a multilayer (bulk, 0.75 eV) to a monolayer (1.89 eV) as a consequence of quantum confinement side effect [1, 27, 38-46]. The monolayer possesses high carrier mobility, good flexibility, and transparency which make it a suitable candidate for fabricating high-performance nanoelectronic and optoelectronic devices such as solar cells [44, 47]. The interaction of the nanosheets in the MoS₂ structure causes the indirect E_g to drop drastically (from point Γ in the VB to an energy minimum point in the CB) [27]. However, this interaction does not have any effect on the E_g of the direct electronic transition path at point K. Previously, it has been reported that the indirect E_g is produced by the d_{z^2} orbital of Mo and the p_z orbital of S which can be affected by the z-axis interactions between the layers [27]. On the other hand, direct E_g is not affected by this interaction because it is made up of orbitals which are localised on the xy plane which is parallel to the layer plane [27, 58-51]. In terms of the optical properties, a wide absorption peak of NbSe₂ occurs at the edge of the visible

region [37]. The absorption band of the colloidal dispersions of NbSe₂ depending on the type of solvent used ranges from 400-500 nm [35].

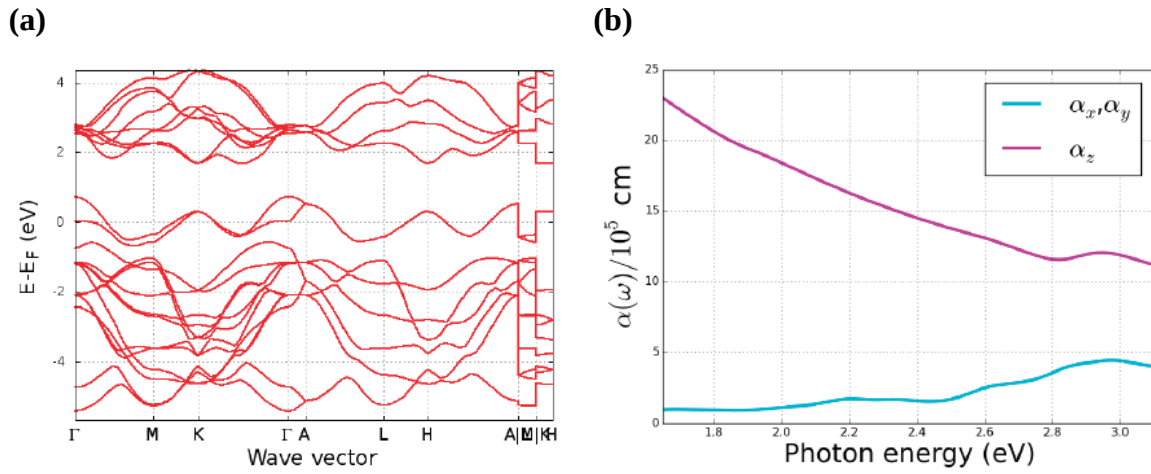


Figure 2.6: (a) Electronic band structure of NbSe₂ and (b) Absorption coefficient of NbSe₂ within the visible range [33].

2.1.3 Nb₂Se₉ properties

Nb₂Se₉ is a semiconductor which crystallises in a triclinic phase [7]. Semiconductors have fascinating and unique properties compared to their bulk due to the limitation of their carriers to a specific volume, which is the same size or smaller than the Bohr radius [52, 53]. Nb₂Se₉ is a new 1D material made up of periodically stacked single-chain atomic crystals (SCAC) which form the inorganic bulk of the crystals due to strong covalent bonds within the chain and weak van der Waals interaction between the chains, as shown in **Figure 2.7 (a)** [27]. It is similar to the structure of NbSe₂ but it has chains and not polymeric sheets. Each Nb₂Se₉ chain is made up of ...Nb₂Se₄-Se₅-Nb₂Se₄-Se₅... sequence along the c-axis as shown in **Figure 2.7 (b)** [7, 27]. Nb₂Se₄ forms a cage, each Nb atom is surrounded by one Se₅ and two Se₂ units thus coordinated to eight Se atoms [7]. Therefore, Nb can be considered to have bicapped-trigonal prismatic coordination around it. The Nb atoms form non-linear chains because of the alternating long and short bonds with distances of 3.76 Å and 2.89 Å, respectively. The electronic properties of this chalcogen-rich material strongly depends on the difference between these Nb-Nb bond distances. Therefore, the associated activation energy increases with an increase in the difference in the distances where the d¹ electrons of the Nb⁴⁺ ions are involved in a strong d¹-d¹ bond [7].

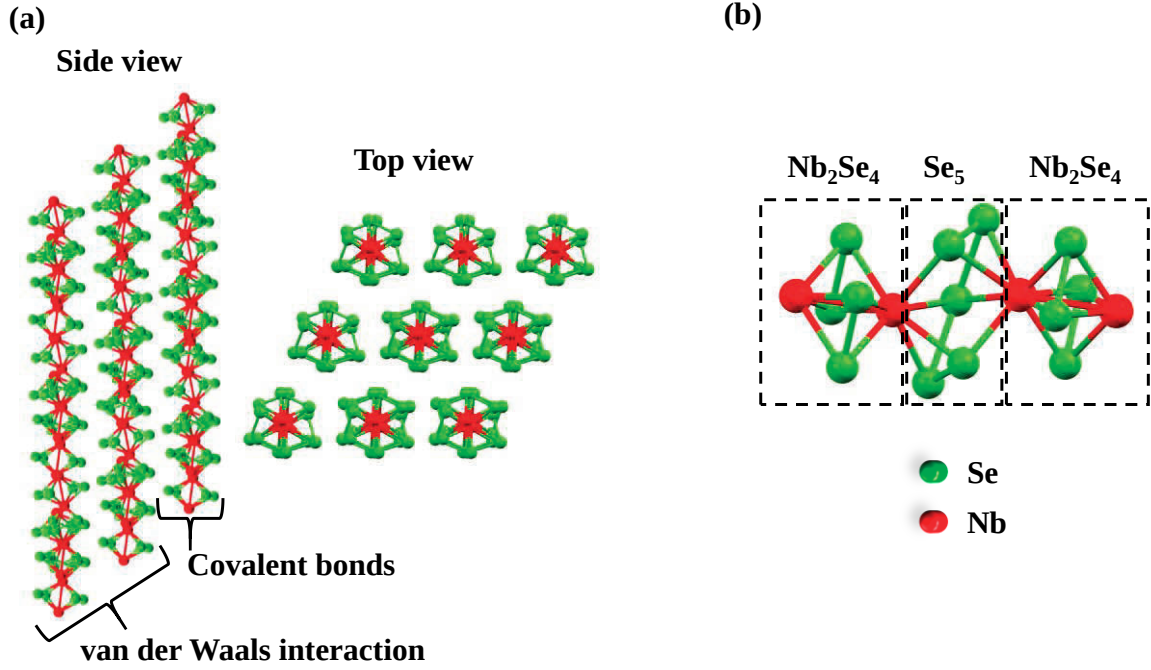


Figure 2.7: (a) stick-and-ball crystal structure of Nb₂Se₉ (side and top view) and (b) a single unit cell of Nb₂Se₉ illustrating the sequence within a SCAC.

The band structure of the bulk which is composed of up to 21 stacked single-chain atomic crystals (SCACs) is an indirect E_g (0.78 eV) [27, 54]. Lee *et al.* discovered an indirect to direct bandgap transition with a reduction of SCACs where they predicted a single chain to have a E_g of 1.20 eV [27]. **Figure 2.8** shows the band structures of the bulk, septuple (0.91 eV), triple, double, and single chain systems indicating the transitions. The bulk Nb₂Se₉ had an indirect E_g between point X and N, whereas all the SCAC bundles had direct bandgaps. The shape of the VB was similar for the bulk and 1D systems that is, maximum energy occurred at point X and the minimum at point Z|N. However, the energy at point Z|N in the CB was maximum in the bulk but minimum in the 1D systems. A difference in the bulk and 1D system was observed at point X. When the number of chains decreased all the energies at point X and Z|N in the CB increased. However, the change in energies between point X and Z|N with the change in dimensions (3D to 1D septuple) was different. That is, the energy change at point X was not significant whereas at point Z|N it was significant. This means that the interaction of the SCACs has a different effect on the energy at point X and Z|N, and also that the spatial arrangement of orbitals corresponding to X and Z|N was different [27].

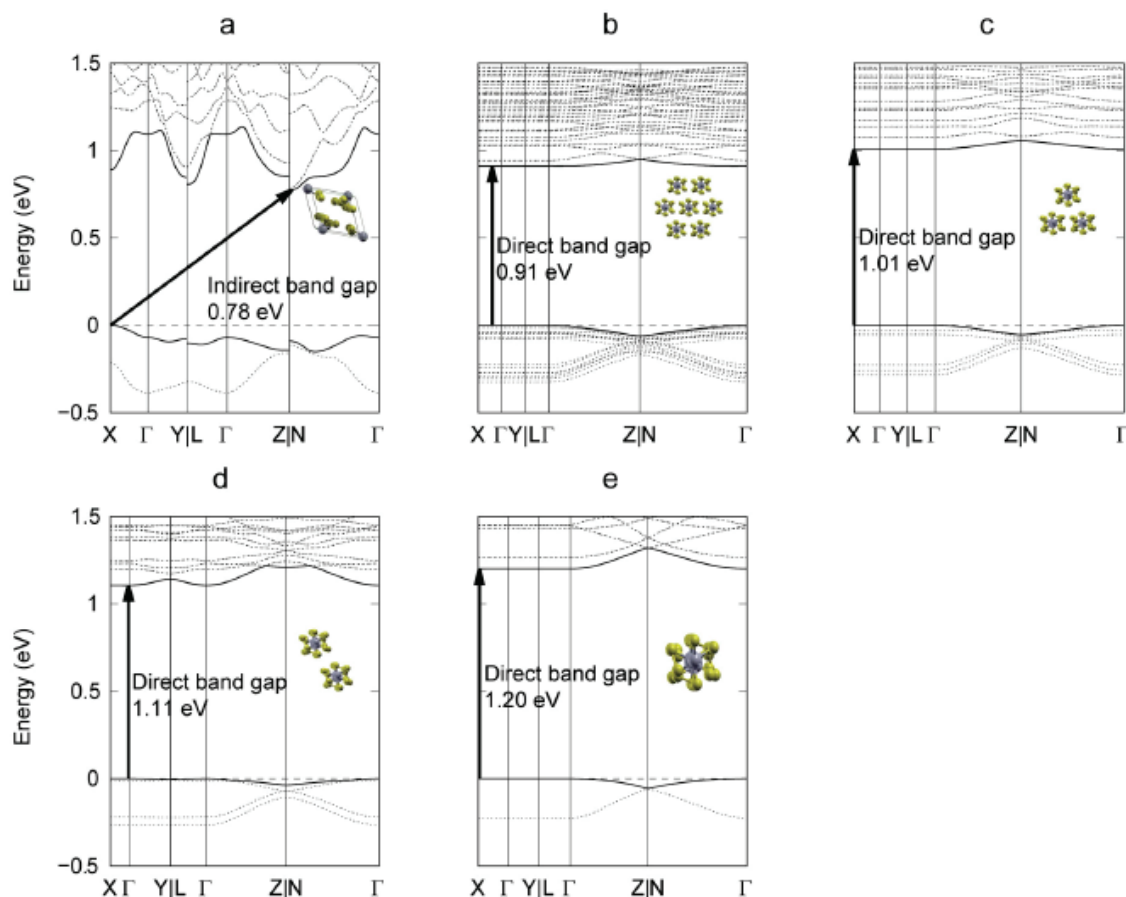


Figure 2.8: Band structure of (a) bulk, (b) septuple, (c) triple, (d) double and (e) single SCAC Nb₂Se₉ showing the transition from an indirect E_g to a direct E_g when the number of chains are decreased [27].

2.2 Synthetic techniques used to synthesise transition metal chalcogenides

Several synthetic techniques have been used to synthesise TMCs to date. There are two approaches that can be used to synthesise these NPs namely: physical approach and chemical approach. The physical approach is a “top-down” process which involves breaking down bulk material into NPs, such as liquid exfoliation. The chemical approach however, is a “bottom-up” process which involves the formation of the NPs “atom by atom” or “molecule by molecule” [55], such as solid-state and solution-based synthesis. Currently, research has been based on making colloidal dispersions of the NPs or using methods that deposit the NPs on a glass substrate. A short review of the various synthetic techniques used to synthesise TMCs, specifically Nb₂Se₉ and NbSe₂ NPs will be done.

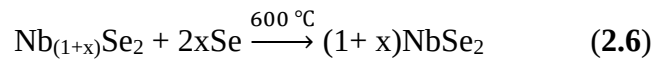
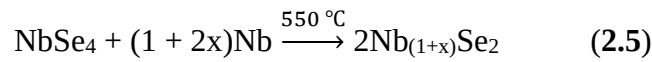
2.2.1 Liquid exfoliation

This technique involves sonicating bulk TMDCs into few- or mono-layers in a solvent and does not involve any heat and is also insensitive to air therefore has the potential to be scaled [29, 35, 56]. The method works effectively in the case where the bulk material has a layered structure (e.g. exfoliation of graphene) such as a series of MX_2 transition metal dichalcogenides (TMDs) (e.g. $M = Nb$, $X = Se$) [35]. For example, Artemkina *et al.* prepared colloidal di- and trichalcogenides in two steps. Firstly, the bulk material was prepared in an evacuated sealed quartz ampoule containing powdered Nb and Se (at 400 °C for 24 h, followed by 800 °C for 7 days). Then liquid exfoliation of the bulk materials in various organic solvent was undertaken. The bulk material was sonicated in an ultrasound bath for 3 - 12 h, then centrifuged and ready for characterisation. These colloidal dispersions were stable with crystallinity and structure of the bulk materials still retained and produced without additional surfactants [35]. As such, they were successful in producing colloidal dispersions that can be used for application as thin-films because the integrity was not lost throughout the process. Chae *et al.* also used exfoliation to separate the bulk Nb_2Se_9 material into single chains by using 16 commonly used solvents [29]. In order for liquid exfoliation to work in this case of Nb_2Se_9 , the solvents used need to have a medium dielectric constant of 10 to 30 and surface tension in the range of 30 to 40 mJ m⁻². For TMDCs however, it has been reported that they have been successfully exfoliated in medium polar solvents with surface energy between 30 and 40 mJ m⁻² [29, 57].

2.2.2 Solid-state synthesis

Solid state synthesis only involves solids, no solvent or surfactant is required. Not only is it used to synthesise NPs but single crystals as well [35, 26, 58]. Artemkina *et al.* used this technique to synthesise $NbSe_2$, $NbSe_3$, NbS_2 and NbS_3 NPs before performing the liquid exfoliation step [35]. Chae *et al.* also used this technique to synthesise Nb_2Se_9 by adding Nb and Se powder into an evacuated quartz tube and heated the mixture up in a furnace at 800 °C for 72 h [29]. Similarly, to Artemkina *et al.* they also exfoliated the bulk material in order to obtain SCACs using various solutions. In order to obtain Nb_2Se_9 instead of $NbSe_2$ or even $NbSe_3$ as an end product, they used a high Nb to Se ratio of 1:200 [59, 60]. Also similar to TMDC, Nb_2Se_9 nanorods have also been prepared by isolating the SCACs from the bulk crystal structures [27]. Nb_2Se_9 was successfully synthesised by the flux method of growing crystals in the liquid phase of Nb and Se in an evacuated quartz tube which was placed in a furnace at 700

°C for 3 days [27, 61]. The resulting dark-grey Nb₂Se₉ nanowires had a width of 100 nm to 10 μm and a length ranging from 10 μm to 10 mm [27]. The nanowires had axially cleaved parts because of the weak-interaction between the units of Nb₂Se₉ SCACs. It has also been proven that the Nb₂Se₉ crystals can be exfoliated into SCACs [27, 54]. Zhang *et al.* also managed to synthesise Nb₂Se₉ NPs by adding a ball-milled mixture of powdered Nb and Se in a sealed reactor which was placed in a furnace and heated to 450 °C [58]. However, when the reaction temperature was increased to 600 °C NbSe₂ nanoplates were obtained [58]. Therefore, it can be assumed that Nb₂Se₉ can be converted to NbSe₂ and this transformation is said to follow the route proposed by Zhang *et al.*:



Zhang *et al.* were not the only ones who discovered this transformation, Guo *et al.* [62] referred to Nb₂Se₉ as an intermediate of NbSe₂ formation. They used a solvothermal method followed by an annealing step. Their ‘intermediate’ was obtained after NbCl₅ and elemental Se was added to degassed OLA where the mixture was heated to 280 °C for 4 h. Then after washing and drying the intermediate, it was annealed at 450 °C for 3 h and resulted in NbSe₂ nanoplates.

2.2.3 Solvothermal synthesis

Hydrothermal and solvothermal synthesis are solution-based techniques. The difference between them is that hydrothermal method uses aqueous solvents and solvothermal uses organic solvents. The advantage of using these synthetic routes is that they provide flexible chemical processing with excellent control over size and morphology [63]. More specifically, organic solvents help with the manipulation of the nucleation and growth process which in turn affects the properties of the NPs [64-67]. Such control can result in the desired optical, electronic and structural properties which are suitable for various application designs [68]. For example, Guo *et al.* made use of a facile and reductant-free solvothermal method to synthesise NbSe₂ nanorods and nanosheets as explained [62]. The difference in the morphology was due to the cooling rate during synthesis which affected supersaturation as such affecting the

nucleation and growth process [62]. Although they were successful in synthesising NbSe₂ in different structures even, they use too much metal precursors, very long reaction times and involved more than one reaction step.

2.3 Colloidal synthesis

One of the most effective ways for controlled synthesis of NPs is the use of solution-based techniques, where the NPs precipitate out a homogenous solution. As such, it is extremely important that the process and formation of the NPs is understood. The colloidal synthesis method is a synthetic technique that uses various chemical processes such as thermal decomposition, sol-gel approach and chemical reduction to produce the metal and chalcogenide atoms required for the desired NP. The thermal decomposition process requires organometallic precursors along with high boiling organic solvents, where the organometallic precursors are able to decompose at elevated temperatures. The colloidal synthesis method in this study was inspired by the work done by Chestoney *et al.* [69]. They were able to synthesis TMCs NPs however the obtained morphology was not monodispersed [69]. The biggest challenge is identifying and controlling the kinetics of the precursors that will lead to precipitation as well as understanding the theory behind the nucleation and growth of the NPs. Reviews of the different processes of how nucleation and growth of NPs are formed from solution-based synthesis have been reported [70-73]. For this study, the best way in which this theory can be described is by the work done by Dinegar and LaMer [74, 75], which has been discussed below.

2.3.1 Nucleation

Nucleation is a process where nuclei (seeds) act as prototypes for the growth of NPs which can be usually identified by a change in colour of the solution or formation of a precipitate during a chemical reaction [70]. There are two types of nucleation process, homogeneous nucleation and heterogeneous nucleation. Homogeneous nucleation occurs when nuclei of the same size are formed, whereas heterogeneous nucleation occurs much easier because there are existing nuclei. The formation of homogeneous nuclei can be described thermodynamically by looking at the total free energy of the NP. Gibbs free energy is defined as the sum of the surface free energy and the bulk free energy. For a spherical cluster, the Gibbs free energy (ΔG) is expressed as:

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma \quad (2.7)$$

$$\Delta G_v = - \frac{k_B T \ln(S)}{v} \quad (2.8)$$

Where r is the radius, ΔG_v is bulk free energy of the crystal and γ is the surface energy. ΔG_v depends on temperature (T), supersaturation of the solution (S), Boltzman's constant (k_B) and the molar volume (v) indicated in equation (2.8). A plot of the Gibbs free energy with respect to the radius in **Figure 2.9** shows the effect of the surface energy on the positive term and the effect of the Gibbs bulk free energy on the negative term. There is a maximum Gibbs energy at the critical cluster radius denoted by r_c which refers to the smallest radius of a particle that is stable in solution. Therefore, if the radius of the cluster is less than r_c then the cluster of particles is unstable and will re-dissolve in solution. If the radius of the cluster is greater than r_c then the cluster of particles is stable and growth is favoured [24, 70, 76]. Therefore, growth will only occur once the cluster of particles is stable and precipitates out in solution. Solving for r_c from equation (2.9), let $d\Delta G/dr = 0$ therefore

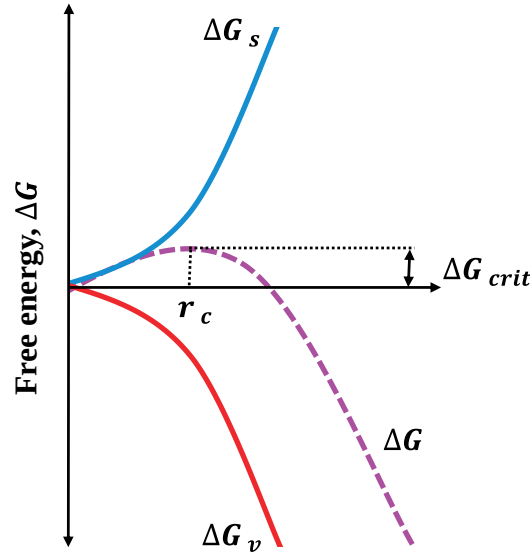


Figure 2.9: Free energy diagram for the nucleation process.

$$r_c = \frac{-2\gamma}{\Delta G_v} = \frac{2\gamma v}{k_B T \ln(S)} \quad (2.9)$$

The rate of nucleation for N particles at time t can be expressed by the Arrhenius equation where the energy barrier for nucleation is the activation energy, thus nucleation must be a statistical process where the nucleation rate dN/dt is expressed by:

$$\frac{dN}{dt} = A e^{\left(\frac{-\Delta G_c}{k_B T}\right)} \quad (2.10)$$

$$\frac{dN}{dt} = A e^{\left(\frac{16\pi\gamma^3 v^2}{k_B^3 T^3 (\ln(S))^2}\right)} \quad (2.11)$$

Therefore, the rate of nucleation is dependent on supersaturation (which has the largest effect), temperature and surface energy (affected by surfactants) of the particles according to equation (2.11) [70].

2.3.1.1 LaMer's nucleation theory

LaMer *et al.* described homogeneous nucleation as a process where after supersaturation there is a burst of nucleation which results in the formation of many nuclei with the same size [70]. Supersaturation during a chemical reaction can occur due to an increase in temperature or a rapid decrease in temperature which will cause a decrease in the solubility of the solute, evaporation of the solute or even super-cooling [77-80], followed by crystal growth without the formation of new nuclei. They described it as a three-step process shown in **Figure 2.10**. The first step involves the decomposition of the precursor which results in the formation of monomer, an increase in monomer concentration which continues until the solution has reached a critical supersaturation (C_s). In the second step, saturation continues to increase until the level of C_{min} is reached which means the energy barrier of nucleation has been overcome and that is when the burst of nucleation occurs. In the third step, the nucleation process stops because the monomer concentration decreases which decreases the supersaturation level. At this stage, the monomers diffuse to the nucleation site and the nuclei begin to grow. This theory is relevant to and only explains the scenario where the resulting NPs are monodispersed [70].

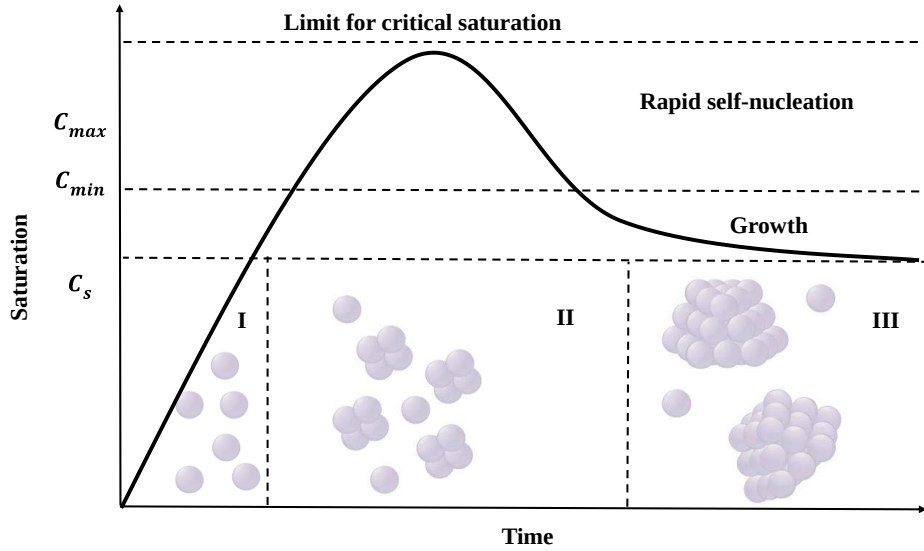


Figure 2.10: Three-step process of LaMer's nucleation theory.

2.3.2 Growth

The growth of NPs depends on two mechanisms: the reaction of the surface and the diffusion of the monomer to the surface [70]. Growth mechanisms can be used to explain heterogeneous growth where the resultant NPs are polydispersed [81]. The manner in which growth of the NPs occurs can be best described by Ostwald ripening. In this process, the smaller particles are unstable and dissolve in the solution (because of their high solubility and surface energy) thus allowing larger particles to grow even more. This is due to the thermodynamic instability of the small particles which are on the surface of the crystal. Therefore, the molecules in small particles will detach themselves and move into solution where they will be attached to larger particles which are more stable. This will continue to a point where the resultant NPs have a large size average. Therefore this phenomenon cannot be used to describe a case where there is a monodispersity of the NPs, as such the burst in the nucleation step plays a crucial role. Another possible mechanism is the Finke-Watzky two-step mechanism where nucleation and growth occur simultaneously [70]. The initial nucleation step is slowly followed by the autocatalytic growth of the NPs which is not governed by diffusion of the monomers. Intra-particle growth is a ripening process involving diffusion of the monomers along the surface of the nanomaterial which results in a change in morphology over time [70].

2.3.2.1 Anisotropic growth

The resulting morphology of the NPs formed after nucleation depends on the surface energy of the exposed crystallographic facets [81]. As such, isotropic and anisotropic growth of the

NPs depends on the surface energy of the exposed crystallographic facets. Isotropic growth is a phase where the surface energy of the exposed crystallographic facets is the same and results in spherically shaped NPs. However, if the surface energy of the exposed crystallographic facets is different, the resulting morphology of the NPs is more complex. The most favoured crystallographic facet will dominate depending on whether the reaction is thermodynamically controlled, kinetically controlled or the balance between the two [24]. **Figure 2.11** shows a potential energy graph of the competitive reactions, where C is the thermodynamically controlled reaction which has a more stable product and D is the kinetically controlled reaction with a lower E_a [82]. The rate constant is exponentially dependent of the E_a . If there is a balance between the two then the molecules will experience different states multiple of times and eventually accumulate at the most stable state [82]. The crystallographic facet exposed in the growth medium influence the final morphology of the NPs [24]. As such, non-centrosymmetric crystal structures are naturally polar therefore they tend to grow anisotropically into rods under kinetically controlled conditions [24].

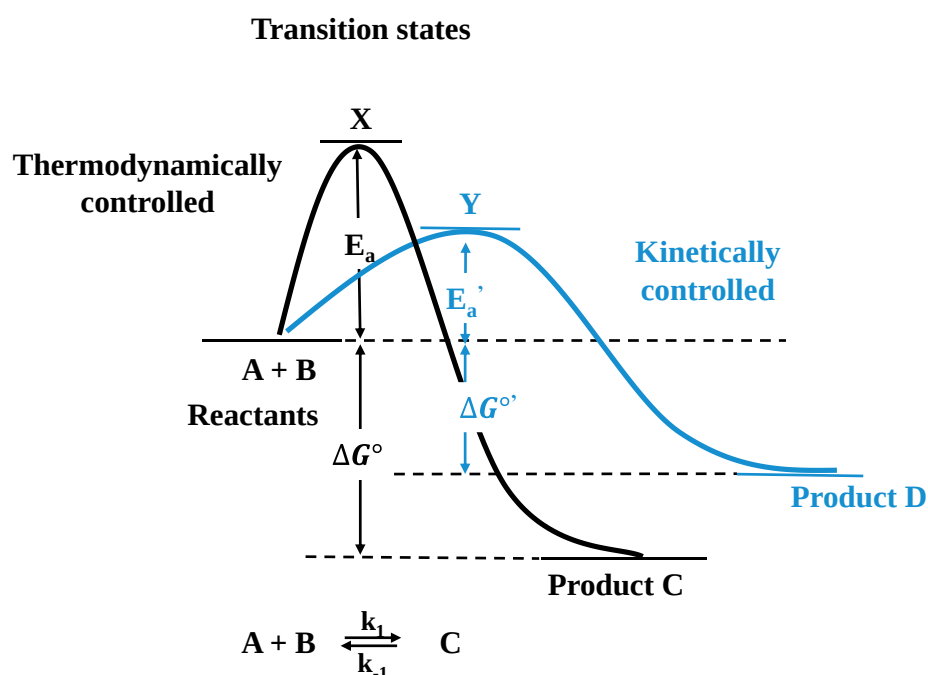


Figure 2.11: Potential energy graph of the two competitive reactions: thermodynamically and kinetically controlled.

2.3.3 NP morphology and size

Wulf and co-workers developed the Wulf construction method for determining the equilibrium shape of a crystal [83]. This method shows that there are certain planes which are preferred

because of their lower surface energy and surface area thus determining the morphology of the NPs. The method has been used previously to predict the morphology of the NPs by determining their thermodynamic equilibrium state. However, there have been cases where the method had failed to predict the morphology because the shape was not the most favourable thermodynamically stable morphology. This is for cases where the NPs have a complex morphology or even defects [82]. After investigations on this, an alternative growth process was identified which occurs by aggregation called orientation attachment. Orientation attachment involves a spontaneous self-attachment of nanocrystals resulting in a coalescence growth with particles that share the same crystallographic orientation, as such NPs result with a morphology produced from a random or orderly orientation. This mechanism not only can it explain the formation of anisotropic NPs and NPs with irregular shapes but also for NPs with defects as a result of epitaxial aggregation (the particles form a chain) [82].

An example of this scenario is with 2D structures simply because there are other synthetic parameters that force the NPs to result in the non-favoured thermodynamic morphology [83]. Defect-induced anisotropy is an important factor that has an influence on anisotropic growth of 2D NPs, an example of this is when there are twin plane defects in metal NPs that result in the formation of nanoplates and nanoprisms [84]. Kinetic effects can also have an effect on the morphology of the NPs. The growth rate can also determine the morphology of the nanocrystals. An increase in growth rate will cause the high energy facets to determine the morphology over the rapid addition of the precursor. A decrease in growth rate causes high energy facets to grow faster [85]. The growth rate also depends on the nature and reactivity of the precursors used. Apart from that, temperature and the ligand also have an effect on the growth and can also affect the morphology. Temperature does not only affect the growth rate but affects the manner in which the precursors decompose and the ligand assemblies. For naturally layered materials i.e. 2D structures, their morphology is governed by the Wulff construction method [85]. Consequently, growth will occur in the direction of the preferred plane.

2.3.4 Effect of the precursors

Colloidal synthesis involves the decomposition of precursors to form monomers which increase until the energy barrier for nucleation is reached, nucleation occurs and these monomers react with each other and finally, the NPs grow. Therefore, the types of precursors used play a vital role. The quicker the decomposition of the precursor and formation of the

monomer, the quicker nucleation will occur which will influence the morphology of the NPs [86]. There are two extremes, a high flux of the monomer favour the kinetic control and leads to anisotropic growth (1D structure e.g. rods) whereas low flux of monomer favour the thermodynamic control and leads to isotropic (3D structure e.g. spheres) growth. Under kinetic control, the rate of growth depends on the reaction rate between the incoming monomer and surface sites [24]. The reactivity of the monomer is governed by how quickly these precursors can decompose [86]. This process can be expressed using a chemical equation:



Where P is the precursor, M is the monomer formed after decomposition and k_f is the formation rate/rate constant of the process [86]. Assuming that the process is a first order reaction, the rate constant will depend on the temperature and activation energy which can be expressed as:

$$\frac{d[M]}{dt} = -\frac{d[P]}{dt} = Ae^{\left(\frac{-E_a}{RT_v}\right)}[P] \quad (2.13)$$

Where A is a prefactor, T_v is the temperature of the solution at any given time and E_a is the activation energy. Since the formation of the monomer depends on the temperature of the solution and activation energy which is related to the binding energy of the ligands bonded to the monomers. Therefore the reactivity of the monomer is inversely proportional to the E_a of the reaction. Embden *et al.* reported three scenarios which can predict the overall yield and size distribution of the NPs [24, 86]:

- (i) High reactivity (low E_a): the binding energy of the ligands to the monomer is low, therefore low or room temperature is sufficient to release the monomers. Rapid formation of the monomers will result in high nucleation and growth rates. As such, this will result in low yields and broad size distribution of the NPs.
- (ii) Moderate reactivity (medium E_a): the binding energy of the ligands is slightly higher than that of the high reactivity scenario. Therefore, slightly elevated temperatures are required to release the monomers. Formation of the monomers, in this case, occurs quickly but for a short period of time followed by growth, thus the rate of nucleation and growth are balanced out. As such, this results in a good yield and a narrow size distribution of the NPs.

- (iii) Low reactivity (high E_a): the binding energy of the ligands is relatively high, therefore relatively high temperatures are required in this scenario. The rate at which the monomers are formed will be slow, thus the formation of nuclei will also be slow which will result in the formation of small and large nuclei. This will lead to the Ostwald ripening which was explained above in section 2.3.2. As such, this will result in low yield and broad size distribution of the NPs.

Therefore, the choice of precursors used is very important and the desire is to obtain a good yield with the narrow size distribution of the NPs. This can be done by making sure the precursors have a moderate reactivity.

2.3.5 Effect of the capping agents

The capping agent also plays a vital role in colloidal synthesis. These organic compounds not only act as solvents but also as surfactants and reducing agents [87]. They bind to the surface of the NPs to prevent oxidation on the surface and aggregation of the NPs to form large clusters [88]. The manner in which they bind to the NPs directs the way in which growth will occur because some facets are hindered. The type of organic solvents used in colloidal synthesis has terminal electron donating groups such as an amine ($-NH_2$), thiol ($-SH$), hydroxyl ($-OH$), phosphine ($-PR_3$) and carboxylic acid, for example, oleylamine (OLA), 1-dodecanthiol, octanol, trioctylphosphine and oleic acid as shown in **Figure 2.12** [88]. There are three ways in which the capping agents can bind, by chemisorption, electrostatic interaction and hydrophobic interaction which is depicted by the terminal-functional group [89]. The capping agents are in a dynamic process of binding and unbinding to the NPs [70]. Each terminal-functional group has an affinity to a specific facet on the NPs, as such, affecting the reactivity of the monomer, which in turn controls the morphology of the NPs [70, 71]. Moreover, they allow the colloidal synthesis to operate at elevated temperatures in order to decompose the precursors [89].

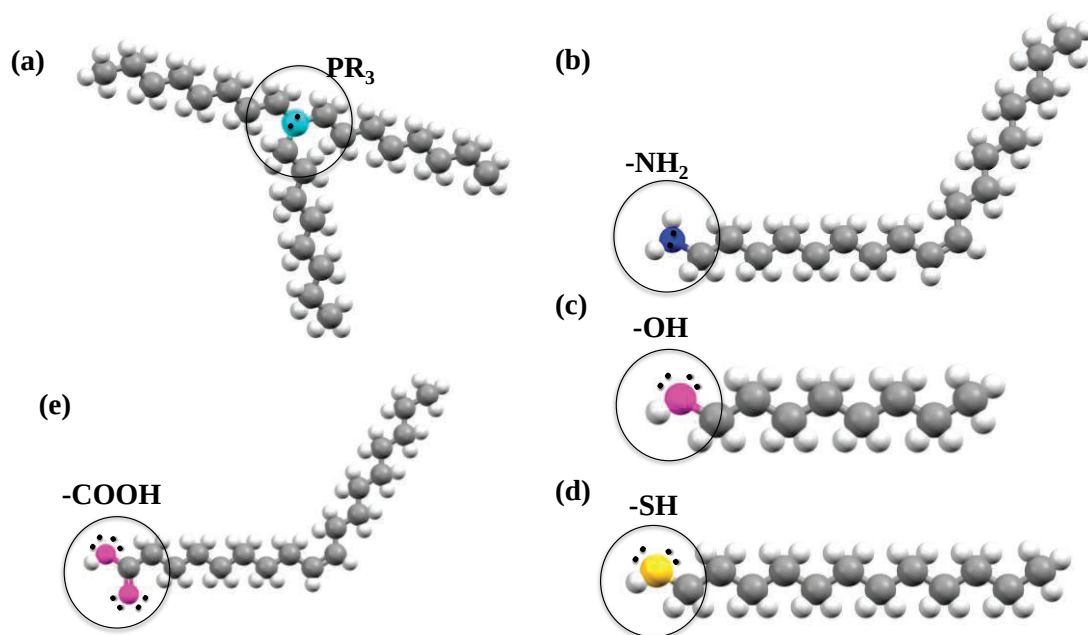


Figure 2.12: Molecular structure of the different organic solvents used in colloidal synthesis with their donor atoms highlighted, (a) trioctylphosphine, (b) OLA, (c) 1-octanol, (d) 1-dodecanthiol, and (e) oleic acid.

2.4 Dye-sensitized solar cells

The first DSSC was discovered in 1991 by Michael Gratzel and Brian O'Regan. The DSSC is a simple photoelectrochemical cell that replicates the photosynthesis process in plants. This cell had initially an efficiency of 7.1 – 7.9%. Through consistent research, the efficiency of DSSCs has reached a maximum of 13% in 2016. DSSCs differ from conventional semiconductor devices because the function of light absorption and charge carrier transport parts are separated [92-95]. Apart from the conductance substrate, DSSCs are composed of three counterparts, namely, the photoanode, the electrolyte and the counter-electrode.

2.4.1 Photoanode

A photoanode is essentially a semiconductor nanocrystalline film (usually TiO_2 or ZnO_2) deposited on a conductive substrate (e.g. FTO or ITO glass) sensitised by dye molecules. It is responsible for the conversion of photons into electrical energy, where light harvesting, electron injection and collection, as well as recombination processes occur. An ideal photoanode consists of a mesoporous semiconductor which provides a high surface area for

the dye to be absorbed. Secondly, the energy levels of the dye, semiconductor, and electrolyte should match. Moreover, the surface area and electronic properties of the material determine the output current of the device. As such, the type of material used as a photoanode plays a crucial role in the performance of the device [92].

2.4.2 Electrolyte

An electrolyte with a redox couple (usually I_3^-/I^-) is responsible for charge transfer between the photoanode and the CE. It is also responsible for the regeneration of the dye and electrolyte itself. An electrolyte consisting of I_3^-/I^- redox couple in volatile solvents are mostly used because of its favourable penetration into the porous film, quick regeneration, and slow recombination.

2.4.3 Counter-electrode

The most crucial component responsible for collecting electrons flowing from the external circuit and also responsible for catalysing the reduction of I_3^- to I^- , is the counter electrode (CE) [62]. Pt is mostly used as a CE because it has good electrocatalytic activity and good stability. However, Pt is a noble metal thus it is scarce and expensive. This poses difficulty in terms of industrialisation, because it is expensive to produce on a large-scale. Therefore, development of Pt-free and highly efficient (DSSCs) is essential for reducing the overall cost of the solar cell [62].

The operation of the DSSC is shown below in **Figure 2.12**. Photoexcitation (when a photon is adsorbed by a dye molecule in the TiO_2 /electrolyte interface) results in an injection of an electron into the conduction band of the TiO_2 from the LUMO of the dye due to an overlap of the bands. For absorption of photons to occur in the visible light spectrum, it is essential that the bandgap of the semiconductor material is of the correct size (i.e. large bandgap). The dye is regenerated by a donation of an electron from the redox electrolyte where the I_3^- is converted to I^- . The Pt-CE completes the circuit by accepting an electron to reduce the redox electrolyte species from I^- to I_3^- . The open circuit voltage is determined by the difference between the Fermi level of the photoanode and the redox potential of the electrolyte. For effective charge separation there are two factors to be considered, (i) the conduction band (CB) of the photoanode must be in alignment with the LUMO of the dye, and (ii) the CB of the photoanode must have a large number of energy states than LUMO of the dye [92-95].

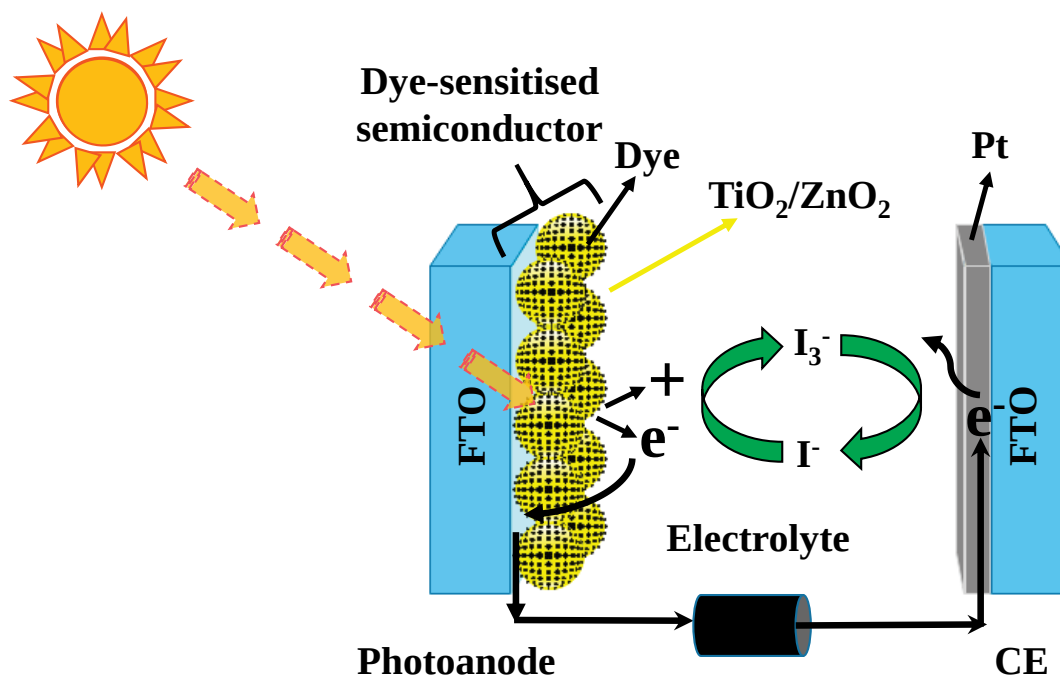


Figure 2.12: Operation of a DSSC.

Hence, much research has gone into the investigation of the dye-sensitisation of semiconductors [95]. Different materials that have the potential to replace Pt, these include carbon materials [96-98], conductive polymers [99-102], composite materials [103, 104] and some inorganic compounds i.e. transition metal nitrides, oxides [107-109] and carbides [110-112]. These substitutes have proven to be competitive alternatives of Pt [62]. Even more recently, TMCs such as MoS_2 and WS_2 which have layered structures have proven to be competitive to Pt-CEs [113-116]. However, TMCs containing selenium (i.e. M_xSe_y , $\text{M} = \text{metal}$) have proven to have a greater PCE than Pt [117]. To date, there has been less Se-based CEs being reported in literature.

2.4.4 Performance of the counter electrode:

Cyclic voltammetry is a technique that is commonly used to study the electrocatalytic activity of CEs in the reduction of triiodide (I_3^-) [62]. The performance of the DSSC depends on the reduction whereas as the oxidation does not have that much effect [118]. An illustration of a cyclic voltammetry and all the useful information that can be extracted is shown in **Figure 2.13**. There are two important components used to compare the electrocatalytic activities of different CEs in CV, namely: peak-current densities (I_p) and peak-to-peak separation (E_{pp}) which are negatively correlated to the standard electrochemical rate constant of a redox reaction

[119]. The negative reduction pair is responsible for I_3^-/I^- and the positive oxidation for I^-/I_3^- (equation 2.14 and 2.15, respectively).

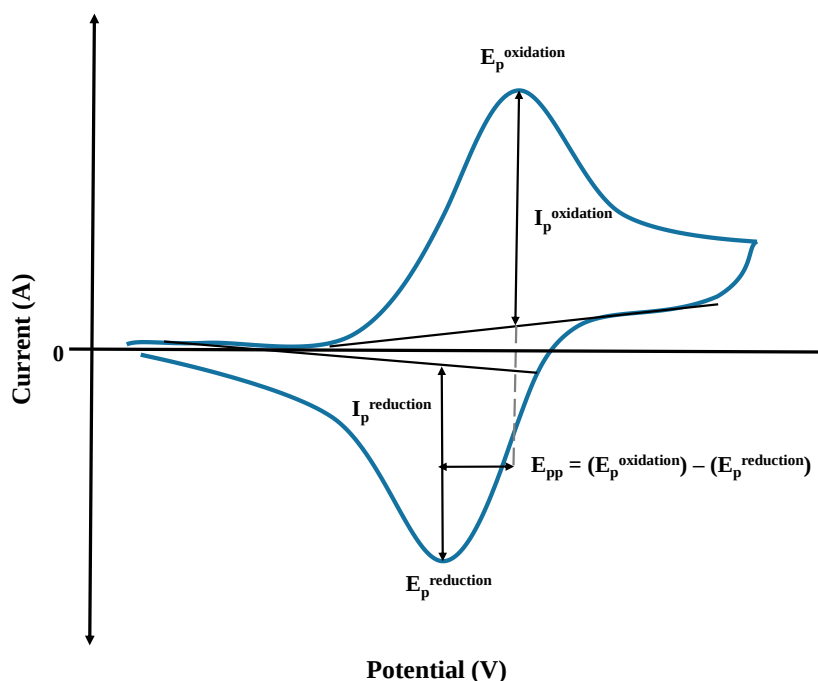
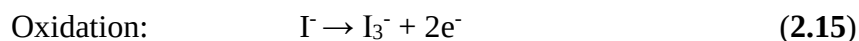
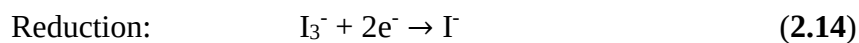


Figure 2.13: An illustration of a typical cyclic voltammogram depicting the peak position (E_p) and peak height (I_p).



The cathodic peak gives information about the reduction velocity whereas the E_{pp} gives information about the reversibility of the redox reaction. The smaller the E_{pp} , the better the reversibility. Guo *et al.* used a reductant-free solvothermal process to produce NbSe₂ nanosheets and nanorods [62]. The profile of the NbSe₂ CE and cathodic peak positions were close to that of CE-Pt indicating that their electrocatalytic reduction of I_3^- is Pt-like. However, the nanosheets CE had a smaller E_{pp} value and similar reduction peak positions to Pt which indicates better electrocatalytic activity and reversibility in the I_3^-/I^- redox reaction. The nanorods CE, on the other hand not so comparable with a E_{pp} value much greater than Pt and lower current density. It has been speculated and proven that nanosheets improve the electrocatalytic activity of the material because of a large specific area and as such speeds up the diffusion of the electrolyte.

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Chapter 3

Shape and phase control of niobium selenide nanostructures by varying reaction parameters

3.1 Introduction

Shape and phase control of nanoparticles still remains a crucial process for successful application in nanotechnology as they affect the overall properties of nanoparticles [1]. Among other techniques, solution-based techniques have been widely used to synthesize nanoparticles (NPs) for the sole purpose of controlling their shape and size [2, 3]. Several reports show that the shape and size of NPs can be controlled by manipulation of several reaction parameters including time, temperature, concentration, types of precursors and capping agents [4-10]. Back in 1993, Murray *et al.* pioneered a controlled synthesis of CdE (E = S, Se, Te) nanoparticles with a narrow size distribution using a simple pyrolysis process [11]. An understanding and manipulation of the nucleation and growth process paved way for a new area in the nanosynthesis [12]. The best way the nucleation and growth process can be described is by the Dinegar and LeMar's theory [13, 14]; this theory has been described in detail in Chapter 2 section 2.3.1.1. This means that the effect of the reaction parameters needs to be evaluated in order to understand the nucleation and growth process of niobium selenide nanomaterials. According to thermodynamic and kinetic premises, above the supersaturation threshold, the infinite nanoparticle growth is spontaneous where the rate of growth can be controlled by changing the degree of supersaturation, temperature and adding an additive (e.g. capping agent) [15]. If particle growth is not controlled, then Ostwald ripening will be favoured which will result in agglomerated nanoparticles [16].

It has also been reported that capping agent-assisted synthetic routes result in very fine nanostructures [1, 10]. These capping agents are said to have a physical or chemical attraction to the molecules lying on the surface of the nanoparticles, thus forming a protective layer around the nanoparticles to prevent them from aggregation or even incorporation of other precursors [1, 12, 16, 18-20], as shown in **Figure 3.1 (a)** such that they attach to active sites during nucleation/growth thus determine the final shape of the NPs. Herein, three different capping agents were varied, oleylamine (OLA), 1-octadecene (ODE) and hexadecylamine (HDA) shown in **Figure 3.1 (b)**. Moloto *et al.* reported that they used HDA as a capping agent which decreased the growth rate as well as the nanoparticle size and improved the quantum

efficiency of photoluminescence for the nanoparticles by passivation of the surface [21-23]. Heteroatom-functionalised long-chain hydrocarbons such as oleic acid (OA), OLA, TOP, and 1-DDT among others have proven to produce good morphology and size distribution by binding strongly to the surface of nanoparticles [24, 25]. Although there is a lot of evidence on the role of a capping agent, the quantitative description remains vague. It has been reported before that an increase in the chain length of the capping agent results in larger particle size [26, 27]. Yang *et al.* used OLA as a surfactant, solvent and reducing agent to synthesize highly luminescent capped-CdSe nanoparticles and discovered that the concentration of OLA affected the concentration and the final particle size [28].

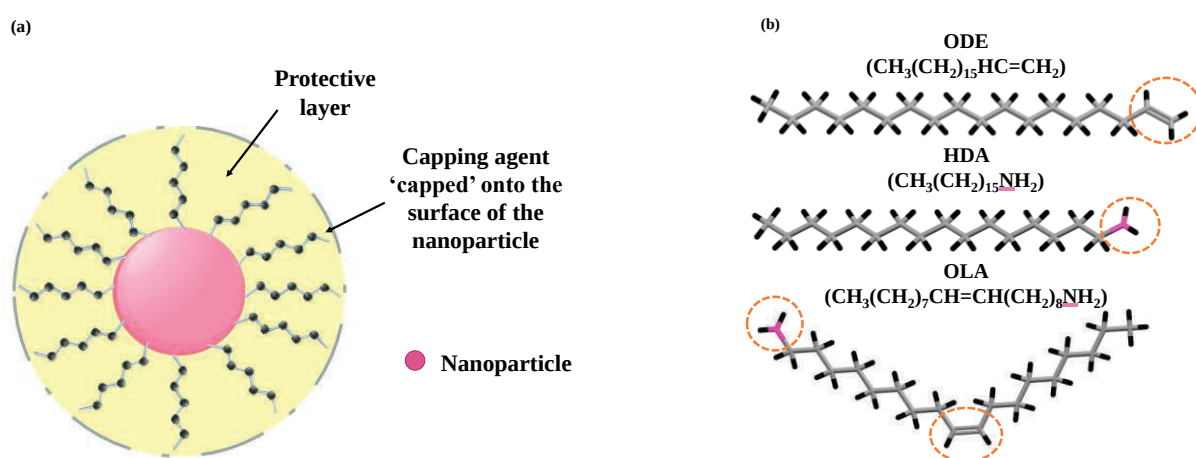


Figure 3.1: (a) an illustration of a capped nanoparticle and (b) molecular structures of the capping agents used in this study: ODE, HDA, and OLA.

In terms of concentration, according to equation (3.1) which shows the relation between the total number of crystals (N_c) with the supersaturation ratio (S) where A and B are positive constants, the higher the concentration of the precursors the larger the number of crystals, therefore, smaller sized nanoparticles will be formed [18].

$$\log N_c = A - \frac{B}{(\log S)^2} \quad (3.1)$$

Concentration tuning can be achieved in two different ways, by changing the volume of the capping agent used or the mass of the precursors [29]. Dehsari *et al.* reported that control over shape and morphology of nanostructures can be achieved by adjusting the precursor concentration. However, they found that the size of the nanoparticles does not automatically

increase with an increase in the precursor concentration [29]. Instead, the size increases to a maximum and decreases with an increase in precursor concentration. This was observed by other researchers as well as i.e. an increase [4, 29-31] and decrease [5, 32] in nanoparticle size. However, the explanation around it is still not clear [29]. Therefore, they argued that two size regimes occur when the precursor concentration is varied but with the volume of the capping agent only one regime occurs. Essentially, it is the ratio of the capping agent to the precursor that played a crucial role [29].

Temperature on the other hand affects the decomposition rate of the precursors, thus affecting the nucleation time shown in **Figure 3.2** as discussed in chapter 2, section 2.3.1 where the image was explained in more detail [33]. The T_2 nucleation time $>$ T_1 nucleation time thus resulting in bigger nucleation radius (r_2). For example, Manzoor *et al.* reported that a decrease in nucleation time results in a good size distribution but the crystallinity of the nanoparticles was compromised [33]. Therefore, the nucleation time has to be perfect so that good size distribution and crystallinity are both obtained. For example, Ghamsari *et al.* found that an increase in temperature caused a decrease in supersaturation, an increase of the nucleus size, an in flux of monomers, the density of the nanoparticles and the growth rate [17, 34].

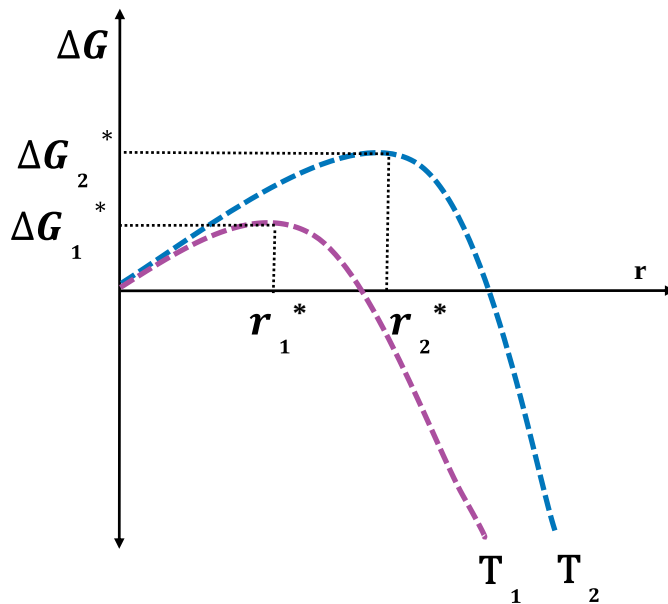


Figure 3.2: An illustration of the effect of temperature on the nucleation time with an increase in temperature from T_1 to T_2 which causes a change in Gibbs free energy as a function of the nucleus radius.

3.2 Experimental set-up

3.2.1 Chemicals

NbCl₅ 99%, 99% elemental selenium powder, 70% oleylamine (OLA), 90% hexadecylamine (HDA), 90% octadecene (ODE), 95% hexane, 96% ethanol, and deuterated-dimethyl sulfoxide (d-DMSO) were purchased at Sigma Aldrich and used without further processing or purification.

3.2.1 Synthesis of NbSe₂ and Nb₂Se₉ nanomaterials

Precursors, NbCl₅ and Se in the mole ratio of 1:4 were added to a three-neck round bottom flask containing OLA that was degassed under N₂ for 15 min. The mixture was further degassed for another 10 min under magnetic stirrer before being heated to the desired temperature. After 120 min, the nanoparticles formed were cooled and washed with large amounts of hexane and ethanol to remove the by-products, air dried and ready for characterisation. Each of the following reaction parameters: temperature, reaction time, concentration and capping agent were varied shown in **Table 3.1**. The concentration of the mixture was varied by varying the volume of the capping agent used.

Table 3.1: Summary of experimental conditions

Effect of	Temperature (°C)	Reaction time (min)	Concentration (M)	Capping agent
Temperature	280	60 and 120	0.125	OLA
	300	60 and 120	0.125	OLA
	320	60 and 120	0.125	OLA
Concentration	320	120	0.167	OLA
	320	120	0.250	OLA
	320	120	0.500	OLA
Capping agent	320	120	0.125	HDA
	320	120	0.125	ODE

3.2.2 Characterization

A Specord 50 AnalytikJenaUV-Vis spectrophotometer was used to carry out the absorption measurements and the nanoparticles were dispersed in hexane and placed into quartz cuvettes

(1 cm path length). The structure and phase of the nanoparticles were determined by Bruker D2 Phaser Powder X-ray diffractometer (XRD) using a $\text{CuK}\alpha$ radiation (λ 1.54184 Å) at 30 kV/30 mA. Measurements were taken using a glancing angle of incidence detector at an angle of 2° , for 2θ values over $10 - 90^\circ$ in steps of 0.026° with a step time of 37 s and at a temperature of 25°C . The morphology and size of the nanomaterials were determined on FEI Technai T12 Transmission electron microscopy (TEM) which was operated at an acceleration voltage of 120 kV with a beam spot size of 3 in TEM mode. TEM samples were prepared by drop-casting the nanomaterial dispersion in hexane onto lacey-carbon copper grids and allowed to dry at room temperature. The 300 MHz Bruker NMR data was used to determine whether the nanoparticles are capped. The samples were dissolved in deuterated d-DMSO.

3.3 Results

3.3.1 Effect of temperature and reaction time

The resultant nanoparticles were characterized using XRD to confirm their crystal phase and purity shown in **Figure 3.3**. After a reaction time of 60 and 120 min, there is a transition from Nb_2Se_9 triclinic phase (PDF 01-078-1383) to NbSe_2 hexagonal phase (PDF 01-070-5612) when the temperature is increased from 280°C to 320°C with the exception of Nb_2O_5 orthorhombic phase (PDF 30-0873) (indicated by ‘*’). There is a decrease in crystallinity of the nanoparticles where the reaction time was increased from 60 min to 120 min, for both 280°C and 320°C because the peaks are broader and less defined. At 300°C , however, the crystallinity increased. There is a mixture of NbSe_2 and Nb_2Se_9 at 60 and 120 min when the temperature was maintained at 300°C . The transition from Nb_2Se_9 to NbSe_2 was also observed by Zhang *et al.* [35] (explained in detail in Chapter 2 section 2.2.2.).

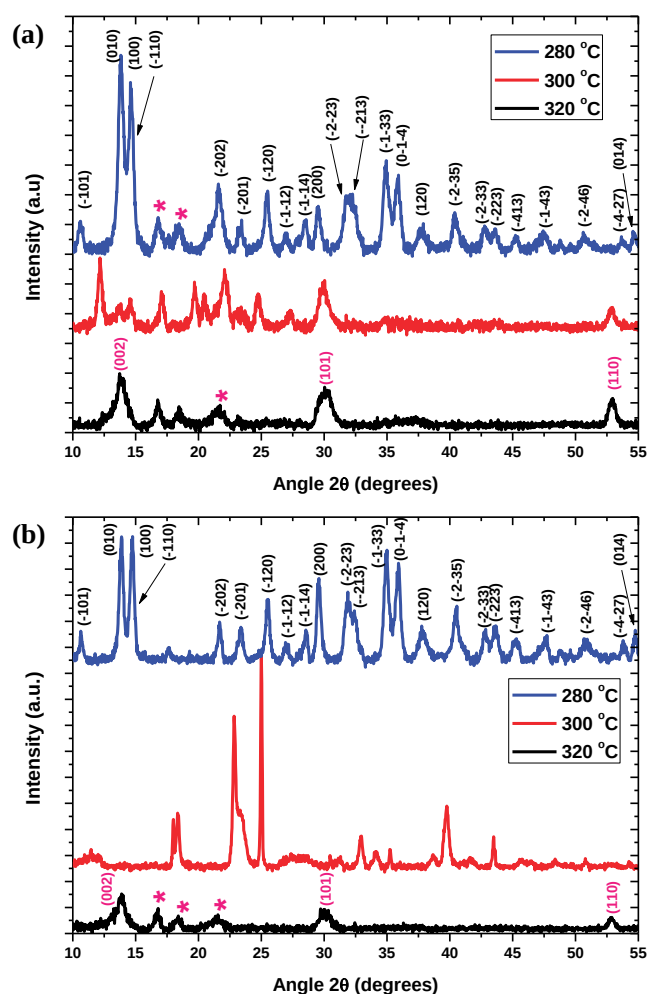


Figure 3.3: XRD patterns of niobium selenide nanoparticles synthesised at various temperatures in (a) 60 min and (b) 120 min; unidentified peaks ‘*’ = Nb_2O_5 .

The morphology of the as synthesised nanoparticles was determined by TEM, shown in **Figure 3.4**. At 280 °C as the reaction time was increased from 60 to 120 min, there was an increase in the monodispersity of the nanorods in terms of length. At 300 °C, there is a mixture of nanorods and nanoflowers after 60 and 120 min. However, the majority of the nanoparticles were nanorods after 60 min and nanoflowers after 120 min. This is an indication that not all nanorods were transformed into nanoflowers, hence the mixture of NbSe_2 and Nb_2Se_9 in the XRD pattern in **Figure 3.3**. As such, the temperature was increased to 320 °C where after 60 min a mixture of nanorods and nanoflowers were observed. In this case, the nanorods have a flake-like morphology. After 120 min, only nanoflowers were obtained. This case is similar to that of 280 °C simply because the particles became more monodispersed as the reaction time was increased. This coincides with the XRD data above because after 120 min there is a transition from nanorods to nanoflowers with an increase in temperature from 280 to 320 °C. And Nb_2Se_9 ,

as well as NbSe_2 , are known to crystallise in the form of nanorods [36] and nanoplates [37] respectively.

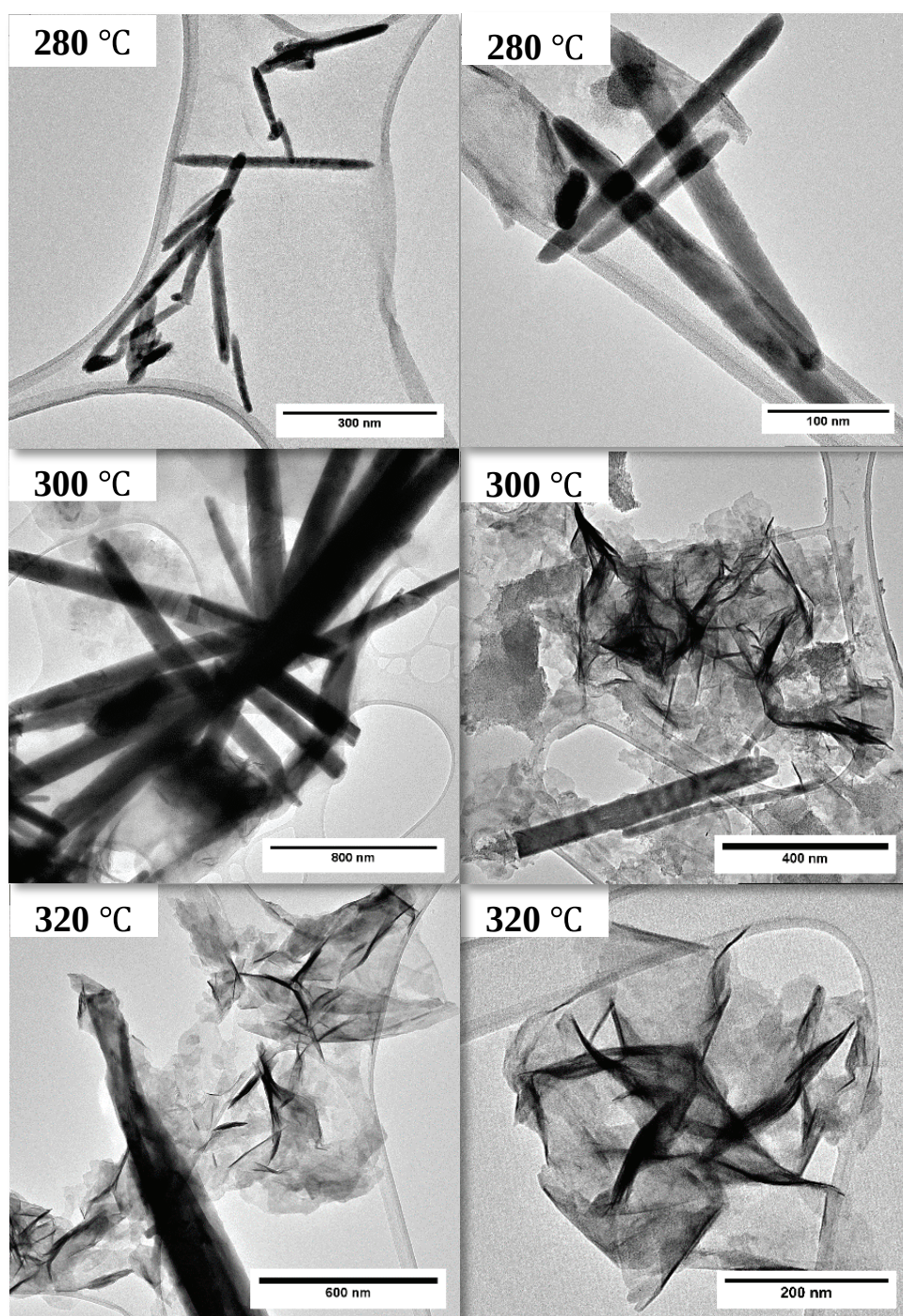


Figure 3.4: TEM micrographs of niobium selenide nanoparticles synthesised after 60 min (left side) and 120 min (right side).

Optical properties of these nanomaterials were determined using UV-Vis absorption spectroscopy, shown in **Figure 3.5**. As the reaction time is increased from 60 to 120 min, the absorption peaks became more defined. At 280 °C, there are two absorption peaks at 399 and 561 nm after 60 min which red-shifted after 120 min to 404 and 565 nm. At 300 °C, there is a blue shift with an increase in time from 610 to 525 nm. And, at 320 °C there is also a red shift with an increase in time from 524 to 575 nm. S. B. Artemkina *et al.* discovered that dispersing NbSe₂ nanoparticles in different solvents excluding hexane resulted in a shift in the absorption peak, they found that the range was between 400 and 500 nm [37].

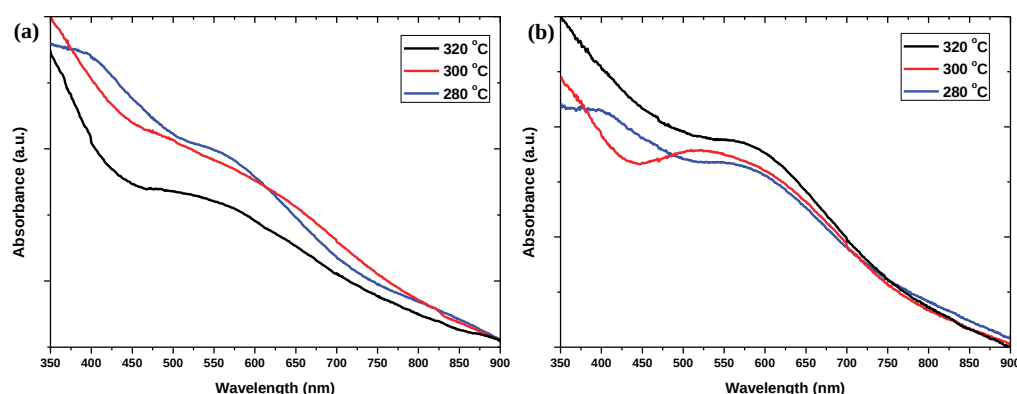


Figure 3.5: UV-Vis absorption spectra of the niobium selenide nanoparticles after (a) 60 min and (b) 120 min.

3.3.2 Concentration

The effect of concentration was further studied. The structural properties revealed by XRD analysis indicated that at a constant temperature of 320 °C and synthetic time of 120 min, an increase in concentration (0.500 M) favoured the formation of Nb₂Se₉ triclinic phase (PDF 01-078-1383) in **Figure 3.6**. The concentration of 0.167 M resulted in a mixture of hexagonal NbSe₂ and triclinic Nb₂Se₉. As it has already been shown in section 3.3.2 that the concentration of 0.125 M favoured the formation of NbSe₂ hexagonal phase.

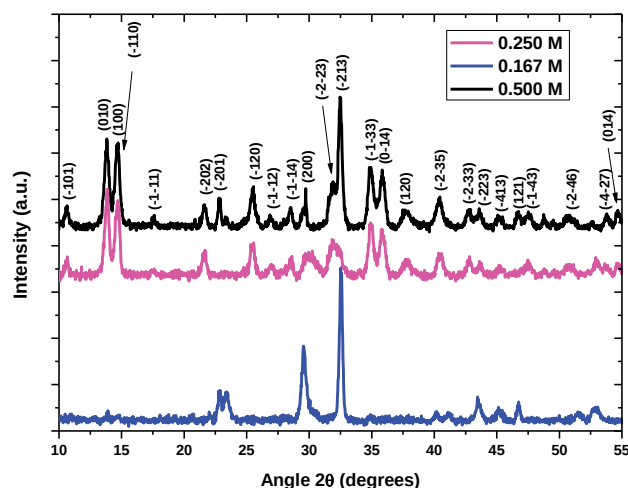


Figure 3.6: XRD patterns of niobium selenide nanoparticles synthesised under different concentrations after 120 min.

The morphology of the synthesised nanomaterials was determined using TEM shown in **Figure 3.7**. The nanorods with Nb_2Se_9 triclinic phase were formed at 0.500 and 0.250 M as shown in **Figure 3.7 (a) and (b)** respectively. Although the nanorods at 0.250 M are flatter in shape than the 0.500 M nanorods. At 0.167 M (**Figure 3.7 (c)**), there is a mixture of nanorods and nanoflowers which confirms the XRD results above (**Figure 3.6**) where there was a mixture of Nb_2Se_9 and NbSe_2 .

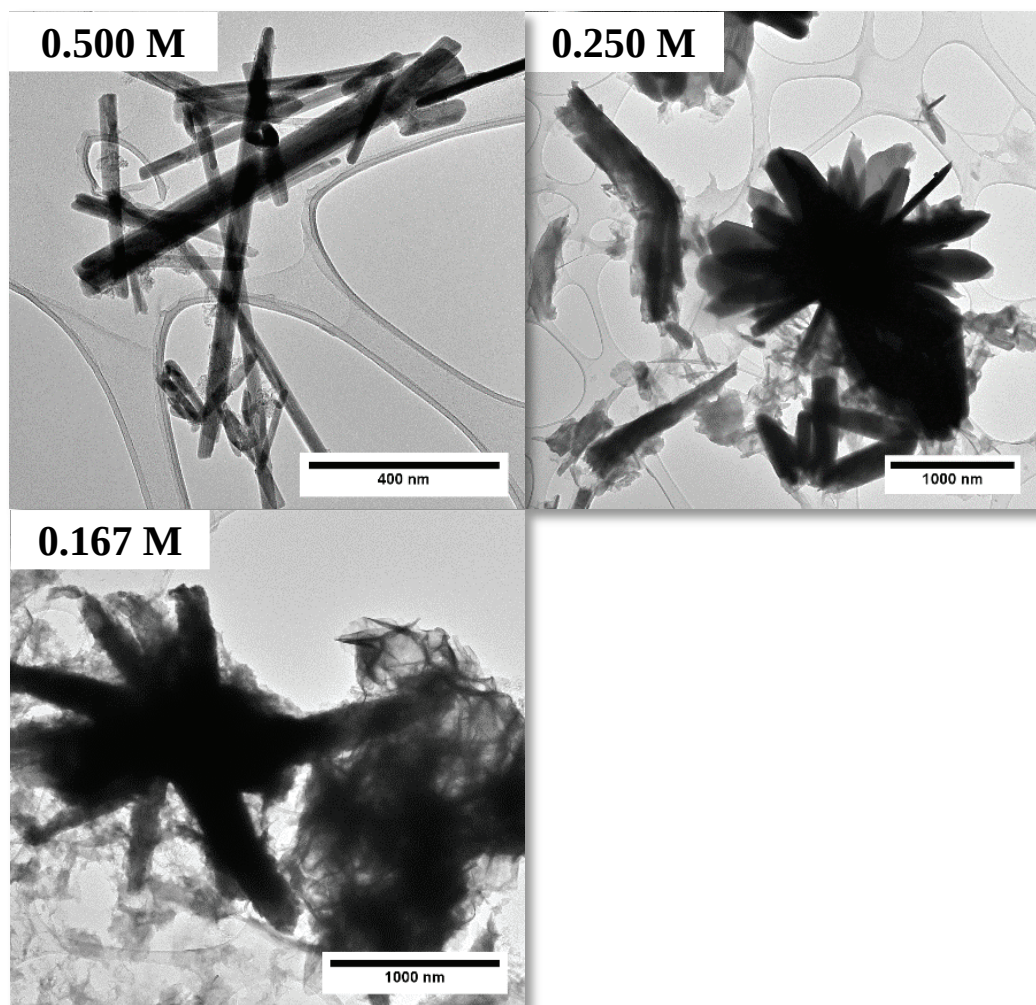


Figure 3.7: TEM micrographs of niobium selenide nanoparticles synthesised under different concentrations.

The optical properties of the synthesized nanoparticles were investigated using UV-vis absorption spectroscopy. The resulting spectra indicated that an increase in concentration results in a decrease in peak tailing shown in **Figure 3.8**. This confirms the decrease in the polydispersity of the nanoparticles shown in **Figure 3.7**. At a concentration of 0.167 and 0.250 M, there are absorption peaks at 586 and 588 nm, respectively. Whereas, when the concentration is increased to 0.500 M two absorption peaks are obtained at 400 and 561 nm.

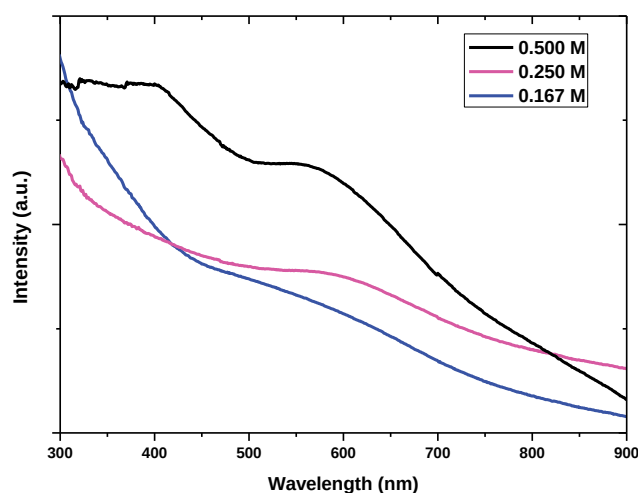


Figure 3.8: UV-Vis spectrum of the particles where the concentration was varied.

3.3.3 Capping agent

The niobium selenide nanoparticles were also synthesized using HDA and ODE to see if the surfactant has any effect on the growth of the nanoparticles. Both capping agents resulted in Nb_2Se_9 triclinic phased nanoparticles (**Figure 3.9**) but OLA resulted in hexagonal NbSe_2 nanoparticles (the XRD pattern is shown above in section 3.3.1.). The HDA peaks were much sharper than ODE peaks which are an indication that HDA nanoparticles have a better crystallinity. This is due to the basicity of the capping agents because they have different donating groups as such they bind differently to the surface of the nanoparticles.

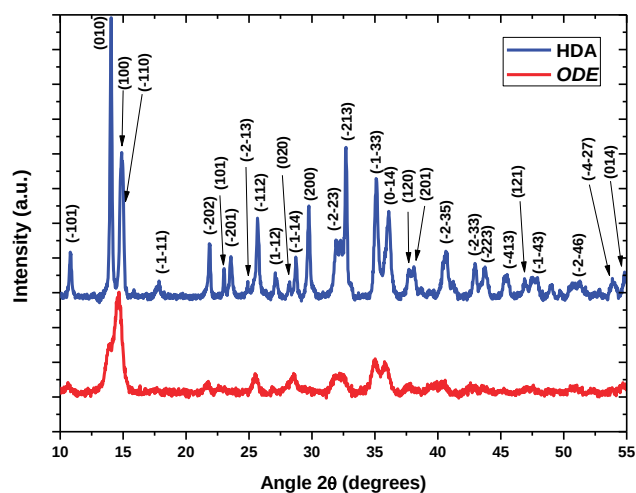


Figure 3.9: XRD patterns of Nb_2Se_9 nanoparticles synthesised using different capping agent HDA and ODE.

The morphology of synthesized nanomaterials was determined by TEM and presented in **Figure 3.10**. The use of both HDA and ODE as a capping agent resulted in the formation of Nb₂Se₉ nanorods. However, ODE nanorods are more monodispersed and narrower than HDA nanorods.

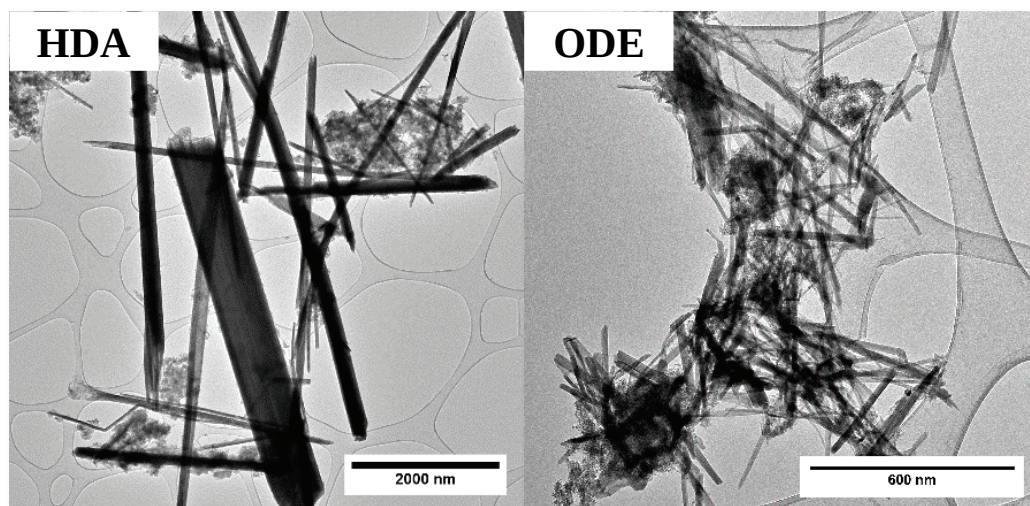


Figure 3.10: TEM micrographs of Nb₂Se₉ nanomaterials synthesised using different capping agents.

The optical properties analysis resulted in an absorption peak at 615 and 812 nm for HDA and ODE respectively shown in **Figure 3.11**. Morphology of these nanoparticles plays a huge role in the optical properties that is a change in morphology results in a change in the absorption peak position, this is confirmed by both the absorption spectra and TEM images in **Figure 3.10**.

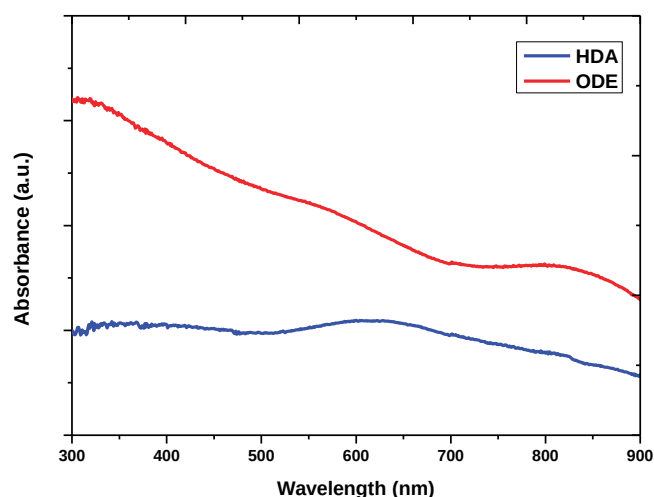


Figure 3.11: (a) Absorption spectra of the Nb₂Se₉ nanomaterials synthesised using different capping agents.

FTIR analysis was performed to confirm if the capping agents are capped onto the surface of the nanoparticles. To confirm the presence of the capping agents, pure capping agents and the nanoparticles were analyzed (**Figure 3.12**). The nanoparticles synthesized using HDA and OLA has the same spectrum. However, the (N-H) and (C-N) at 1593 and 1071 cm⁻¹ bent stretch bands, respectively have disappeared or have lower intensity in the nanoparticles spectra than the pure OLA and HDA. This confirms that there is a change in the structure of the terminal functional group (-NH₂) in both OLA and HDA, shown in **Figure 3.12 (a) and (b)**. This was an indication that the capping agents are capped onto the surface of the nanoparticles because there was a change in the characteristic peaks of the capping agent in the nanoparticles spectra compared to that of the pure capping agent. This can further be confirmed by NMR. The terminal functional group on each capping agent is suspected to be binding onto the surface of the nanoparticles [38]. On the other hand, the -C=C characteristic peaks at 1644 and 2966 cm⁻¹ for pure ODE have decreased in intensity in the nanoparticles spectrum. However, the ODE synthesized nanoparticles had additional peaks between 1800 and 2600 cm⁻¹, apart from the characteristic peaks, that were attributed to the C=O and O=C-H stretching frequencies. These peaks are thought to come about through the oxidation of the capping agent. Evidently, ODE is more susceptible to oxidation, the C=C bond is easily cleaved forming aldehydes and carboxylic acids.

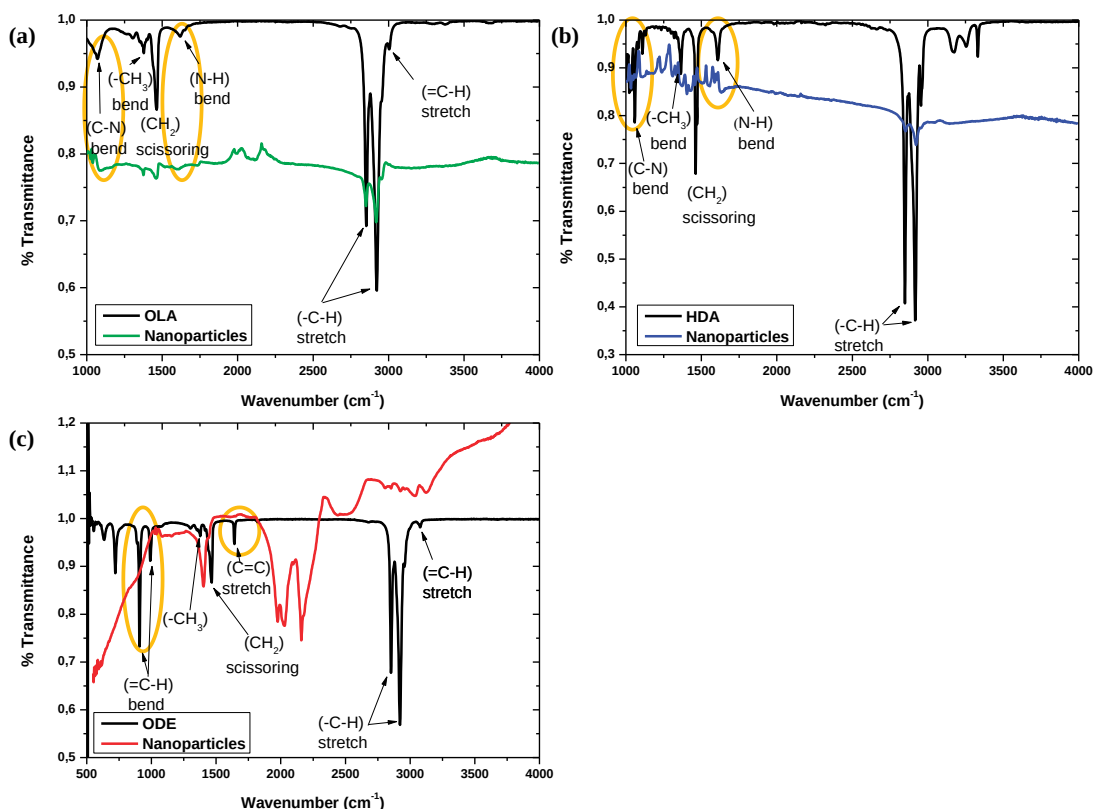


Figure 3.12: FTIR spectra of pure capping agents and capped-niobium selenide nanoparticles; (a) OLA, (b) HDA, and (c) ODE.

NMR was further performed to fill in the gaps of FTIR, pure capping agent and the nanoparticles were run separately. The spectra were compared to each other and the differences were used to determine whether the nanoparticles were capped, similar to FTIR. This is proven by considering two aspects: (i) that the majority resonance peaks of the capping agent and the dispersed nanoparticles have to appear in the same position, and (ii) there should be broadening or a shift in peak position between the capping agent and nanoparticle dispersion which is an indication that the nanoparticles are indeed capped [40, 41]. OLA-nanoparticles have the same resonance peaks as pure OLA; however, the CH_2 resonance peak's (no. 5) at 2.19 ppm intensity has been reduced significantly as shown in **Figure 3.13**. This is an indication that the nanoparticles are capped through the terminal amine because the neighbouring $-\text{CH}_2-$ group peak has changed. Moreover, the OLA-nanoparticles resonance peaks for $-\text{CH}=\text{CH}-$ and $-\text{CH}_2-\text{C}=\text{C}-$ protons intensity had also been reduced significantly at 2.03 and 5.39 ppm.

300 Hz ^1H Spectrum

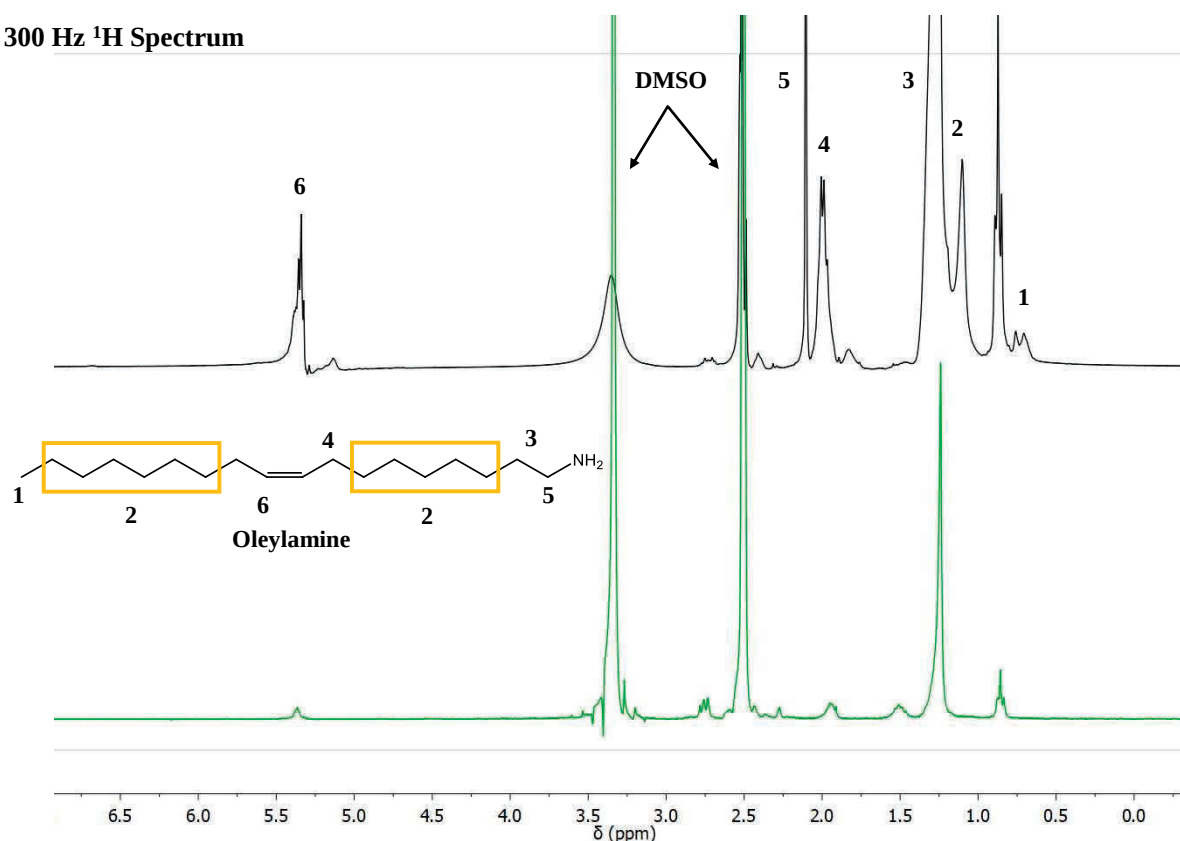


Figure 3.13: NMR spectra of pure OLA and the as-synthesised nanoparticles using OLA as a capping agent.

HDA-nanoparticles have the majority of their resonance peaks in the same position as pure HDA, shown in **Figure 3.14**. However, there is a decrease in intensity of the peaks for the neighbouring $-(\text{CH}_2)_n-$ and $-\text{CH}_3$ groups at 1.26 and 0.88 ppm. There is also an additional broad peak between 7 and 8 ppm, wherein this region $-\text{RONH}_2$ and phenol groups are expected. Using XPS, the capping agent has been shown to be susceptible to the nanoparticles (Chapter 4). NMR spectroscopy, being a more sensitive technique compared to FTIR spectroscopy can thus probe the oxidation.

300 Hz ^1H Spectrum

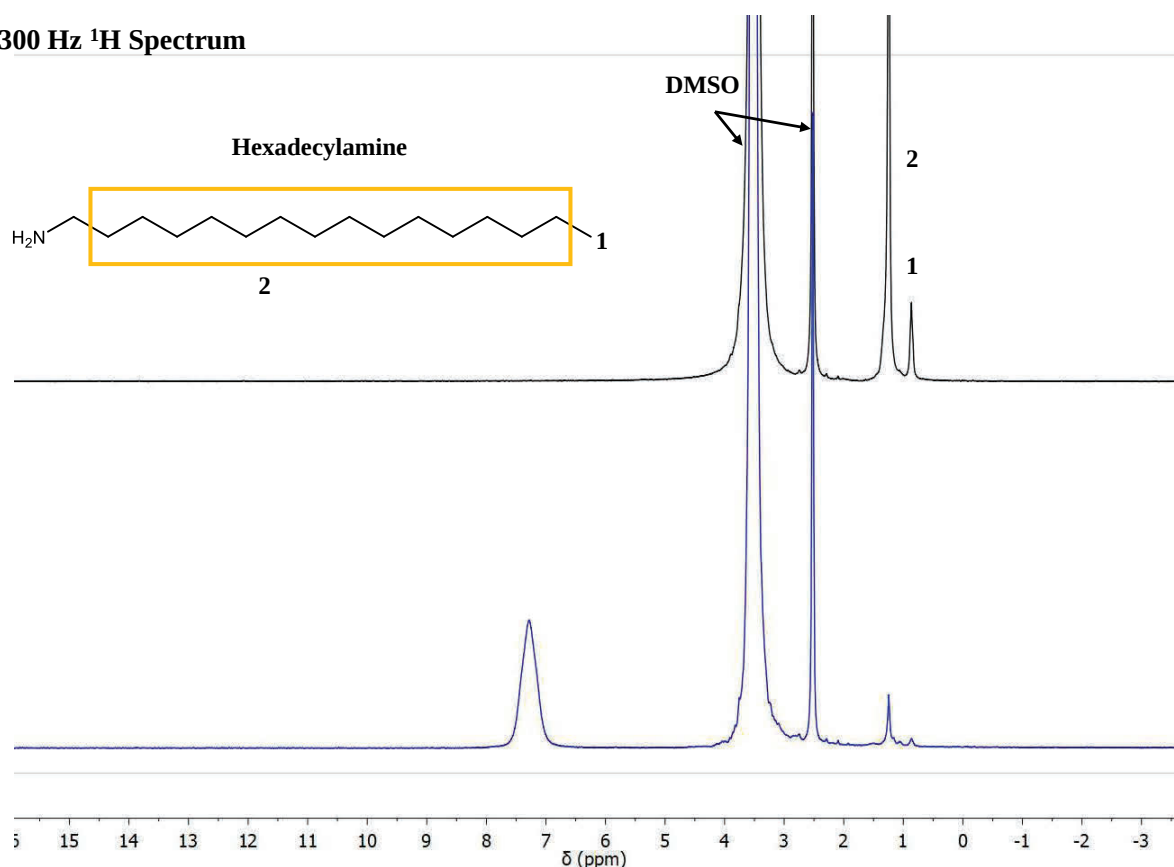


Figure 3.14: NMR spectra of pure HDA and the as-synthesised nanoparticles using HDA as a capping agent.

ODE-nanoparticles have the majority of their resonance peaks similar to pure ODE, however, the $-\text{C}=\text{C}-$ peaks have completely disappeared between 5 and 6 ppm shown in **Figure 3.15**. In addition to this, the characteristic peaks of ODE in the nanoparticles sample all have low intensity compared to the pure ODE. The disappearance of the $\text{C}=\text{C}$ peak is not unexpected as this is the point of oxidation. The $\text{OH}-$ peak of the carboxylic acid is expected to be more downshifted outside the reported spectral window.

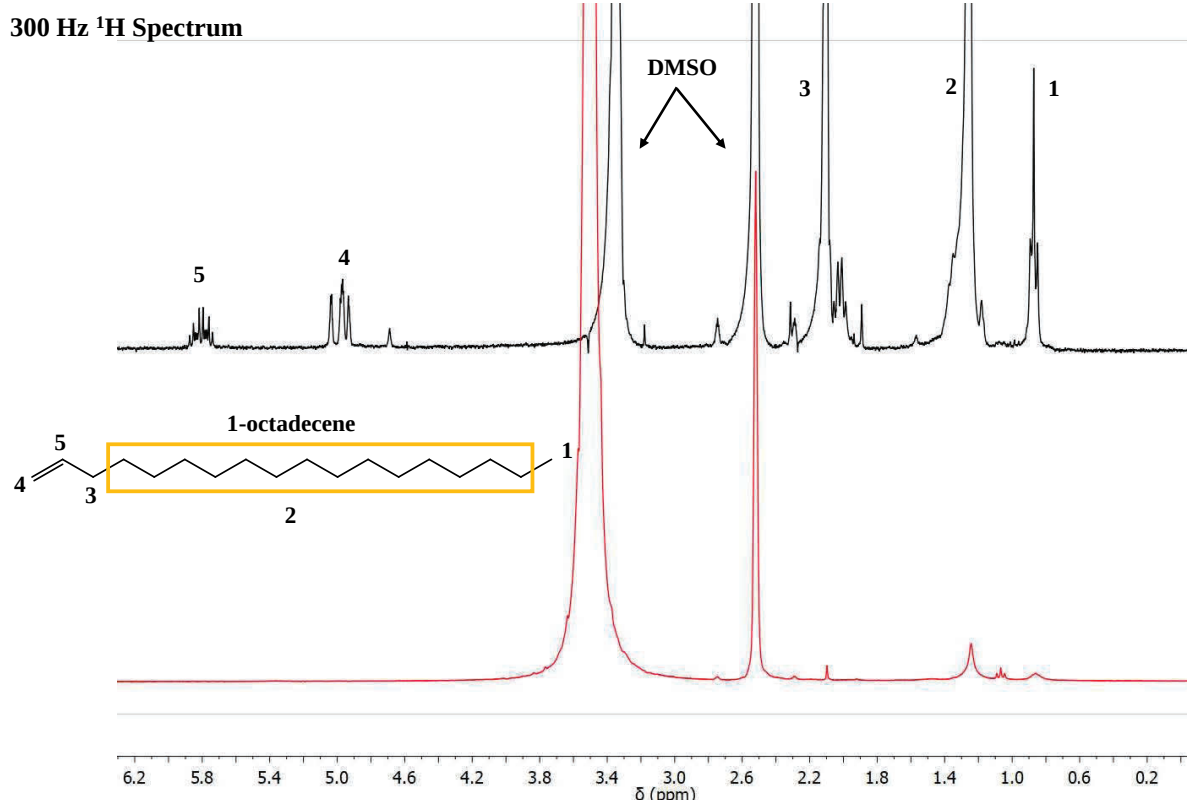


Figure 3.15: NMR spectra of pure ODE and the as-synthesised nanoparticles using ODE as a capping agent.

3.3 Discussion

Reaction time and temperature: Reaction time does not have an effect on the composition of the nanoparticles, because as the reaction time was increased the same composition was maintained but decreased the crystallinity of the nanoparticles. The morphology, on the other hand, became more monodispersed at higher reaction times (i.e. 120 min). Hence, the absorption peaks were more defined (but broad due to the difference in particle size) thus an indication of decreased polydispersity. Essentially, the growth rate of the nanoparticles was affected. With temperature, the higher the temperature the more NbSe_2 nanoflowers are favoured. Temperature has an effect on the rate of decomposition of the precursors, the faster the decomposition the quicker the nucleation process takes place [37]. However, there are two extremes (kinetic and thermodynamic control); a high in flux of monomers favours kinetic control which will result in an anisotropic growth (2D nanoflowers) of the nanoparticles [37]. Therefore, temperature affects both the nucleation and growth processes because not only did the composition of the nanoparticles change but also the morphology. Boris I. Kharisov *et al.* obtained the same results where they found that nanoflowers require higher reaction time and temperature whereas for the formation of nanorods requires lower temperature and reaction

times, a higher concentration of precursors with a decrease in the volume of the capping agent [42]. A decrease in temperature induces supersaturation of an equilibrium mixture containing the growth species [17].

Concentration: Zheng *et al.* reported that a decrease in the solvent essentially decreases the concentration of the surfactants, therefore, the nucleation and growth process can be explained by an increase in the concentration of the monomer in the reaction medium [29, 37]. The concentration of the available monomers at the interface of the nuclei (the crystal growth front) is close to that of the bulk solution because there is less surfactant to stabilize the monomers. Hence, the diffusion distance for the monomers is shorter, which leads to a higher mass transfer and therefore a higher growth rate [29, 37]. In this study, this resulted in the formation of Nb₂Se₉ nanorods. This is because the nanoparticle growth reaction is controlled because the growth rate is mainly governed by reactions on the surface of the nanoparticles [29]. As the amount of capping agent increases (lower precursor concentration), monomer concentration in the solution is decreased which increase the diffusion constant and reduces the growth rate due to less mass transfer in the reaction medium. The nanoparticle growth is, therefore, diffusion-limited [29]; as a result, NbSe₂ nanoflowers are favoured. As such, different optical properties were obtained because of different size, composition, and shape of the nanoparticles was obtained with a change in concentration.

Capping agent: Among the capping agents used in this study, only OLA resulted in the formation of hexagonal NbSe₂ nanoflowers. Akhtar *et al.* reported that capping agents with shorter alkyl chains (i.e. HDA and ODE) may require higher temperatures than 320 °C to obtain FeS₂ nanoparticles [43]. This could be the reason why HDA and ODE do not form NbSe₂ after 120 min. HDA resulted in narrower nanorods than ODE which resulted in a blue-shift in the UV-Vis spectrum. According to Rhadar *et al.*, a blue-shift of the absorption edges of nanoparticles is due to the decrease in particle size caused by the quantum confinement effect of nanoparticles [44]. This is due to the adjustment of their bandgap by quantum confinement. Therefore, the HDA nanoparticles are narrower due to quantum confinement [43]. The donating group on the capping agents also has an effect, because in terms of basicity level (ability to donate electrons) OLA > HDA > ODE. The primary alkylamine (-NH₂) group acts as an electron donor to the surface to stabilize the monomers. Therefore, the additional -C=C- increases the affinity of OLA to the monomers. According to the FTIR spectra for HDA and OLA, these capping agents are capped onto the surface of the nanoparticles through the -NH₂

group because their peaks had a lower intensity than the pure capping agents. Mourdikoudis *et al.* reported that OLA and HDA can act as electron donors at elevated temperatures through their $-NH_2$ functional groups [45]. This was further confirmed by NMR because the characteristic peaks (neighbouring $-CH_2-$ groups) had very low intensities for HDA and OLA. Moreover, OLA and HDA have the potential to coordinate to the metal site through the N group and the chalcogen through the terminal amine via weak hydrogen bonding [46]. According to researchers, ODE is a non-coordinating solvent because it does not contain any coordinating groups [46, 47]. However, according to the NMR results, the characteristic peaks indicate that ODE has been capped onto the surface of the nanoparticles because the peaks had lower intensities. Evident from NMR results is that the capping agents undergo oxidation.

3.5 Conclusion

In summary, we have shown that $NbSe_2$ nanoflowers and Nb_2Se_9 nanorods can be synthesized by controlling reaction parameters such as reaction time, temperature, precursor concentration, and capping agent. Each of these parameters affects either the nucleation process, growth process or both processes which in turn affects the properties and morphology of the nanoparticles. An increase in reaction time affects the growth rate resulting in monodispersed nanoparticles with low crystallinity. An increase in temperature results in the transition from Nb_2Se_9 nanorods to $NbSe_2$ nanoflowers. An increase in precursor concentration results in Nb_2Se_9 nanorods because there is less surfactant to stabilise the monomers. And lastly, all capping agents used were capped onto the surface of the nanoparticles. Moreover, ODE and HDA produced Nb_2Se_9 nanorods and OLA produced $NbSe_2$ nanoflowers.

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Chapter 4

The effect of the Se precursor on the properties of NbSe₂

4.1 Introduction

Over the years, a great deal of research effort has been devoted to the use of colloidal synthesis to make nanomaterials of high quality. Colloidal synthesis involves the thermolysis of precursors in a high boiling solvent to yield nanomaterials with controlled sizes and shapes. The formation of the nanomaterials using the colloidal synthetic method has been said to be governed by the Lamer and Dinegar growth mechanism, where initially, nucleation occurs followed by the growth of the nuclei [1]. In a non-injection colloidal method, all reagents are mixed into a reaction vessel at room temperature and then heated up controllably to initiate the nucleation and growth of the nanoparticles. Shown in **Figure 4.1** is a schematic diagram of the stages of this process and their relation to the temperature of the reaction vessel.

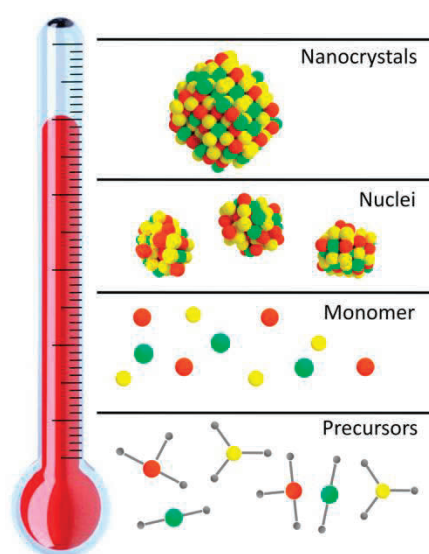
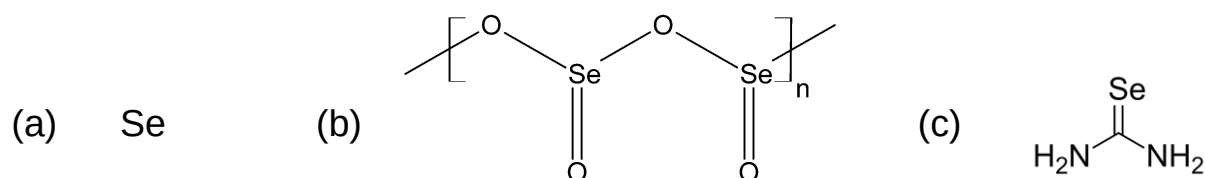


Figure 4.1: Illustration of the processes occurring during a non-injection colloidal method [2].

At room temperature, the reaction mixture is comprised mainly of precursors. As the reaction is heated up, these precursors experience an increased thermodynamic resulting in the formation of monomers. The heating eventually triggers the nucleation process, with continued heating required to grow these nuclei into mature nanoparticles. The growth of the nanoparticles is then arrested by removing the heat. The underlying mechanism for the formation of particles in the non-injection method is therefore similar to that for hot-injection

methods. However, careful consideration to the choice of precursors and ligands is required in the non-injection method in order to ensure that (i) nucleation is rapid enough to generate large quantities of nanosized nuclei within a relatively short period of time and that (ii) appropriate decoupling of the nucleation and growth stages occurs in order to reduce particle polydispersity [2]. The control over the chemistry of precursors and ligands is therefore essential in producing nanomaterials of high quality.

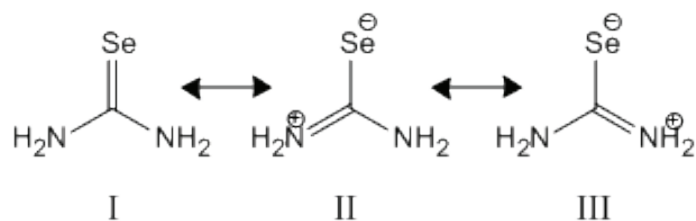
Herein, the selenium precursors were varied in order to investigate their influence on the resultant properties of the nanoparticles. Three precursors were used, namely elemental selenium (Se), selenium dioxide (SeO_2) and selenourea (SU) and their chemical structures are shown in **Scheme 4.1**. Selenium is a non-metal that has similar properties to sulfur and tellurium. It forms several allotropes that interconvert with temperature changes [3]. The structure of black selenium is irregular, complex and consists of polymeric rings with up to 1000 atoms per ring [4]. Black Se is a brittle, lustrous solid. Upon heating, it softens at 50 °C and converts to gray selenium at 180 °C; the transformation temperature is reduced by presence of halogens and amines. The red α , β , and γ forms are produced from solutions of black selenium. They all have relatively low, monoclinic crystal symmetries and contain nearly identical puckered Se_8 rings with different arrangements, as in sulfur [5].



Scheme 4.1: Chemical structures of (a) elemental selenium, (b) selenium dioxide and (c) selenourea.

SeO_2 is a one-dimensional polymer that consists of alternating selenium and oxygen atoms. Each Se atom is pyramidal and bears a terminal oxide group. The bridging Se-O bond lengths are 179 pm and the terminal Se-O distance is 162 pm. The stereochemistry at Se alternates along the polymer chain hence resulting in a syndiotactic polymer [6]. In the gas phase selenium dioxide is present as dimers and other oligomeric species; at higher temperatures it is monomeric. The monomeric form adopts a bent structure very similar to that of sulfur dioxide with a bond length of 161 pm [7].

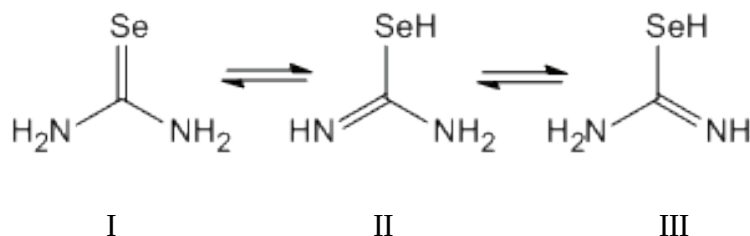
On the other hand, selenourea is an organoselenium compound. This compound features a rare example of a stable, unhindered carbon-selenium double bond [8]. Few studies have been done on selenourea as compared to urea and the oxo-analog of selenourea due to the instability of selenium compounds [9]. X-ray crystallographic measurements on selenourea crystals at -100 °C gave average bond lengths of 1.86 Å and 1.37 Å for C=Se and C-N respectively. Both the Se-C-N and N-C-N angles were measured at 120°, which was consistent with a sp^2 -hybridized carbon. Through these same studies, the existence of Se-H hydrogen bonding in the crystal lattice was confirmed by comparing the O-H and S-H hydrogen bonding found in crystals of urea and thiourea [10]. In addition, the shortened bond length of the N-C and the elongation of the Se=C bond suggested a delocalization of the lone pair on the amines where the Se=C π -bonding electrons were drawn towards the selenium atom, while the nitrogen's lone pair was drawn towards the carbonyl carbon. A similar effect has been observed in urea and thiourea. In going from urea to thiourea to selenourea the double bond is more delocalized and longer, while the C-N σ bond is stronger and shorter. In terms of resonance structures, structures II and III shown in **Scheme 4.2** are more prevalent in selenourea compared to urea and thiourea analogs. However, the lone pair on the nitrogen of selenourea delocalizes only slightly more than the lone pair on thiourea in contrast to a much greater delocalization in going from urea to thiourea. These minor differences suggest that the properties emergent from the delocalized nitrogen lone pair and destabilization of the C=S and C=Se π bond in thiourea and selenourea will also be similar [11].



Scheme 4.2: Structural resonance of selenourea.

Unlike urea and thiourea, which have been extensively researched, relatively few studies have quantitatively characterized selenourea. While the selenone tautomer (I) has been shown to be the more stable form, only qualitative and comparative information on selenourea's tautomerization is available. Comparable to ketones, selenones undergo tautomerism as shown in **Scheme 5.3** [12]. Since the greater delocalization of the lone pair electrons correlates with the selenone product, the equilibrium position of selenourea likely has an equilibrium position

comparable to that of thiourea. Thiourea has been shown to exist predominantly in its thione form at 42 °C in dilute methanol, with the thionol tautomer almost non-existent at neutral pH [13].



Scheme 4.3: Tautomerization of selenourea.

The chemistry of these selenium precursors can therefore influence the resultant properties of the nanoparticles. These selenium precursors have been used in the synthesis of metal selenide nanoparticles and their effect on the resultant properties is tabulated in Table 1 below. Herein, we therefore investigate for the first time, the effect of the selenium precursor on the properties of NbSe₂ nanoparticles.

Table 4.1: Effect the selenium precursor on the morphology of nanoparticles

Nanoparticles	Precursor	Properties	References
CdSe	Se	Prolate particles averaging 35 Å ± 5% in the direction of the (002) wurtzite axis and 30 Å ± 6% perpendicular to the (002) axis.	[14]
	SeO ₂	Spherical CdSe nanocrystals with a diameter of 4.0 nm and a standard deviation of ca. 5%.	[15]
	SU	Pearl-necklace shaped nanowires and multi-width nanowires.	[16]
PbSe	Se	Spherical nanocrystals corresponding to diameters of 3-13 nm with narrow size distributions (σ = 5-7%).	[17]
	SeO ₂	PbSe nanocubes with a side length of 15.9 nm and a standard deviation of 7%.	[15]
	SU	15-3 nm hexagonal nanocrystals .	[18]

MoSe₂	Se	Uniform flower-like morphology and tunable average diameters that range from approximately 50 - 250 nm.	[19]
	SeO ₂	Microspheres with a statistical size of 400 - 600 nm in diameter.	[20]
	SU	Few-layer MoSe ₂ nanosheets	[21]

4.2 Experimental

4.2.1 Chemicals

Niobium (V) chloride 99%, 99% elemental selenium powder, 99.9% selenium dioxide, 98% selenourea (SU), 70% oleylamine (OLA), 95% hexane and 96% ethanol were obtained from Sigma Aldrich and used without further processing.

4.2.2 Synthesis of NbSe₂ nanomaterials

Oleylamine was degassed for 15 min followed by a stoichiometric addition of NbCl₅ and Se or SeO₂ or SU in a three-necked round bottom flask. The mixture with a concentration of 0.125 M was further degassed for 10 min under vigorous stirring before being heated to 320 °C. After 120 min the mixture was cooled and the black precipitate was washed with large amounts of ethanol and hexane mixture, air dried and ready for characterization.

4.2.3 Characterization techniques

The structure and phase of the powdered nanoparticles were determined with the Bruker MeasSrv (D2-205530)/D2-205530 diffractometer using secondary graphite monochromated CuK α radiation (λ 1.54184 Å) at 30 kV/30 mA. Measurements were taken using a glancing angle of incidence detector at an angle of 2°, for 2 θ values over 10 - 90° in steps of 0.026° with a step time of 37 s and at a temperature of 25 °C. X-ray photoelectron spectroscopy measurements were performed with a Thermo ESCA lab 250Xi using monochromatic Al K α (1486.7 eV) x-rays at a power of 300 W with a spot size 900 μ m. The morphologies were studied using a FEI Spirit 120 kV transmission electron microscope (TEM) equipped with an EDX detector operated at an acceleration voltage of 200 kV with a beam spot size of 20 - 100 nm in TEM mode. The particles were dispersed in hexane and drop-casted onto a lacey carbon copper grid. The solvent was then evaporated at room temperature. Scanning electron microscopy (SEM) was carried out on a FEI Nova Nanolab 600 FIB/SEM microscope equipped

with an EDX detector. The powder samples were mounted on aluminium stubs with carbon tape. A Specord 50 AnalytikJena UV-Vis spectrophotometer was used to carry out the absorption measurements. The nanoparticles were dissolved in hexane and placed in quartz cuvettes (1 cm path length).

4.3 Results and discussion

XRD is a useful tool in confirming the formation of the desired product, identifying the phase as well as any lingering impurities. Shown in **Figure 4.2** are the X-ray diffractograms of particles synthesized using the different selenium precursors. The particles synthesized using Se and SeO₂ are indexed to a hexagonal 2H-NbSe₂ phase (PDF 01-070-5612) indicated by the black hkl indices. In addition, there are three high intensity peaks (*) between 2 θ values 15° - 25° indexed to an orthorhombic phase of T-Nb₂O₅ (PDF 30-0873). On the other hand, the particles synthesized from SU precursor were consistent with a rhombohedral phase 3R-NbSe₂ (PDF 01-070-1620). The impurity peaks of Nb₂O₅ are still observed in SU sample however in very small intensities. The peak positions of the 2H-NbSe₂ and 3R-NbSe₂ are similar however there is a small shift towards lower angles for the rhombohedral phase as seen in **Figure 4.2**. In addition, the two phases have different lattice parameters, with $a = 3.45$ and $c = 12.55$ for the 2H-phase while $a = 3.45$ and $c = 18.88$ for the 3R-phase.

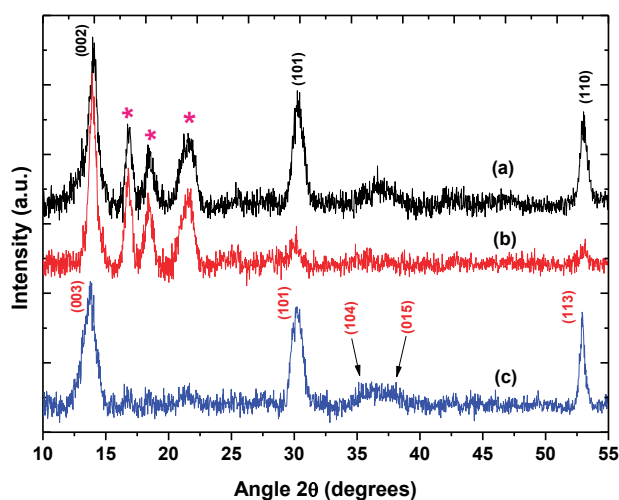


Figure 4.2: X-ray diffractogram patterns of NbSe₂ particles synthesized using (a) Se, (b) SeO₂ and (c) SU precursors (* = Nb₂O₅).

To study the morphological properties of the resultant materials, TEM and SEM studies were undertaken. Shown in **Figure 4.3** are the TEM and SEM images of particles synthesized from

the different precursors. All samples showed sheet-like morphologies. This is consistent with 2D layered materials. From SEM, the sheets are arranged in a flower-like pattern. Most studies on nanosheets usually employ a support such as a substrate in order to obtain flat nanosheets [22]. Colloidal synthesized nanosheets tend to have unfavourable surface energies hence they fold over each other forming architectures such as the nanoflowers in order to minimize the surface energy [23]. Although the focus of many studies has been on the flat nanosheets, 3D assemblies of these nanosheets into nanoflowers have many advantages. These structures have high specific surface area, broad internal space, mechanical stability and easy accessibility to catalytically active sites [24]. The presence of many edge sites has been shown to be advantageous for electrocatalytic applications as the edge sites are more catalytically active than the basal planes of the material [25]. While all the precursors resulted in flower-like morphologies, subtle differences can be observed. The particles synthesized from the Se show smaller nanoflowers with more compact ‘flower petals’. As the precursor is changed to SeO_2 the size of the nanoflowers increases and the petals become less compact. Finally the SU derived flowers are much more spread-out with open petals.

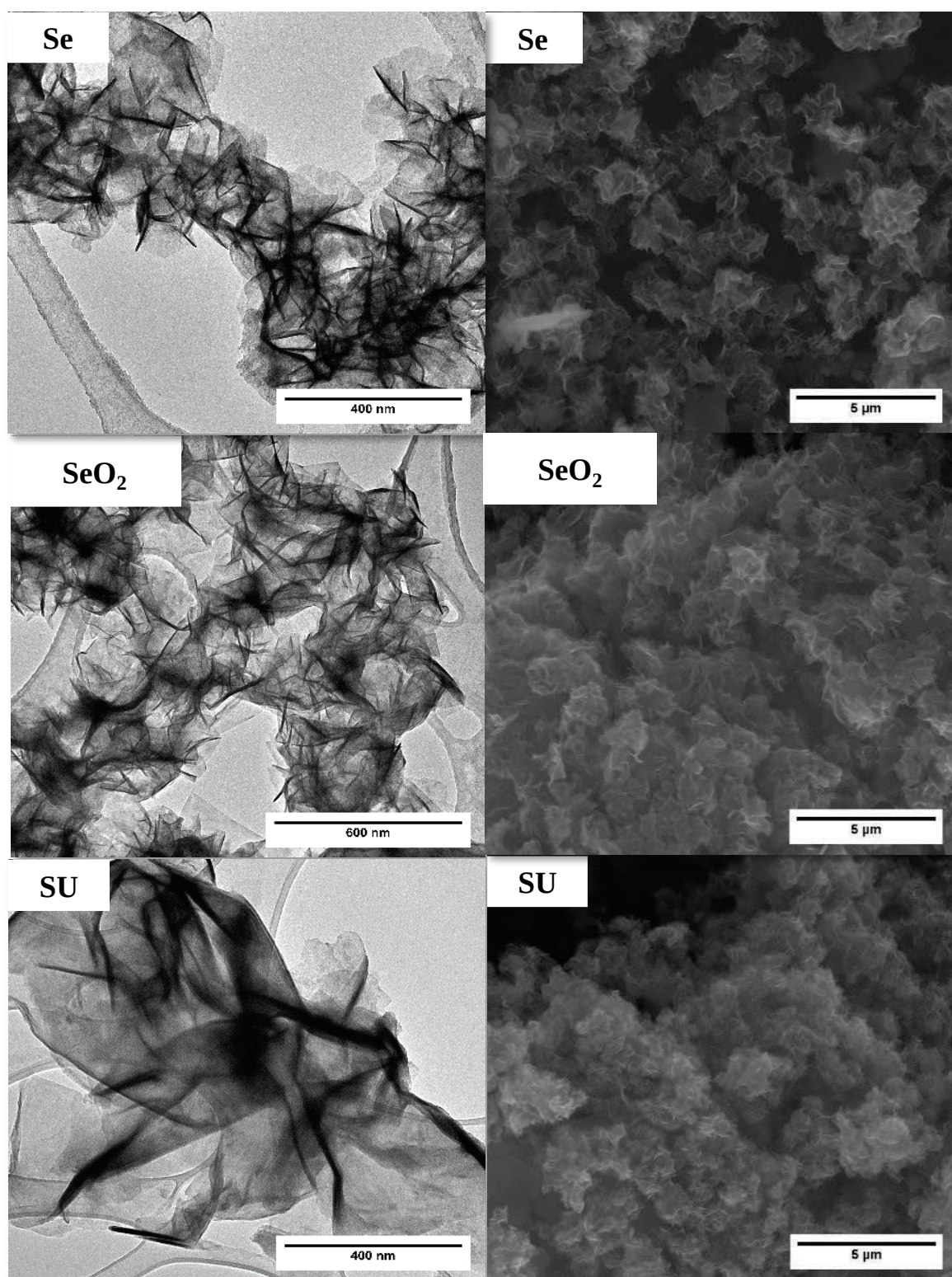


Figure 4.3: TEM and SEM images of NbSe₂ particles synthesized using different selenium precursors.

To study the optical properties of the resultant materials, UV-Vis absorption spectroscopy was undertaken and the results are shown in **Figure 4.4**. NbSe₂ is similar to MoS₂ as they are both

members of the layered materials. In this group of compounds, MoS₂ is one of the typical semiconductors, and the absorption spectrum exhibits characteristic exciton features in the visible region; NbSe₂ on the other hand is a metal, and shows no such sharp features but there is free carrier absorption in the near infrared region [26]. Wilson and Yoffe have also shown by their simple energy band scheme that these properties can be understood in terms of the electron occupation of the top valence band which is made up from the nonbonding d_z^2 orbitals of transition metal atoms. This band is completely filled in MoS₂ and only half-filled in NbSe₂. It is nevertheless reasonable to anticipate that the overall band structures of these two compounds will be similar [26]. The 2H-NbSe₂ nanostructures derived from Se and SeO₂, show an excitonic peak however both the spectra are tailing. The 3R-NbSe₂ derived from SU shows no excitonic peak due to polydispersity. In order to estimate the resultant band gaps, Tauc plots were plotted and the band gaps were extrapolated using the linear regions. The band gap values are approximately 2.5 eV, 2.4 eV and 2.1 eV for Se, SeO₂ and SU derived nanoflowers respectively. These band gaps are firmly in the visible region, with the band gap of SU derived band gap more red-shifted compared to Se and SeO₂. This is not surprising as the SU derived particles have properties slightly different from the other two precursors as evident from the XRD and TEM results.

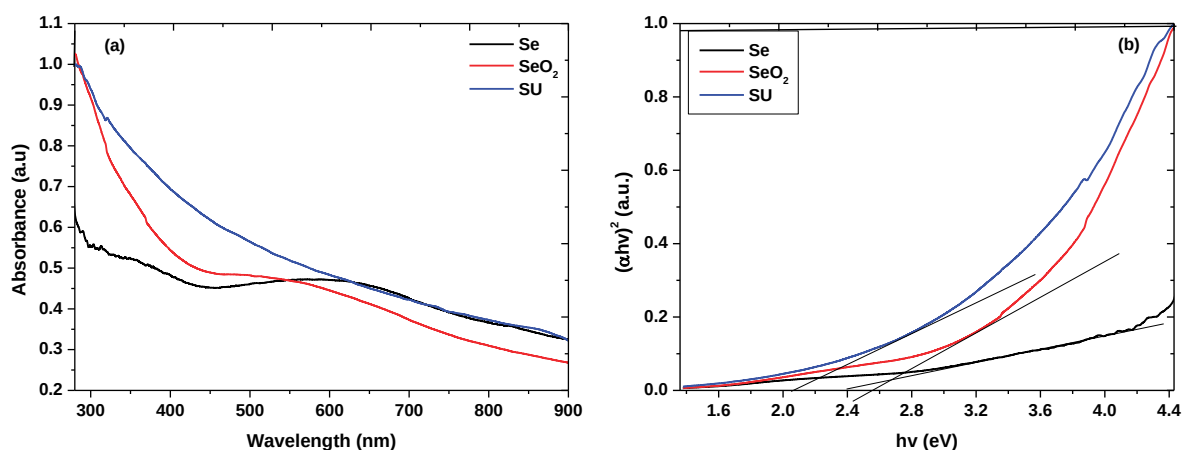


Figure 4.4: (a) UV-Vis absorption spectra of NbSe₂ particles synthesized using different selenium precursors and (b) their corresponding Tauc plots.

To further probe the properties of NbSe₂, the SU derived particles were studied further. From the EDX spectrum shown in **Figure 5.5**, Nb and Se peaks were observed as well as small O peak. The O peak can be attributed to the Nb₂O₅ observed as minor impurity in the XRD.

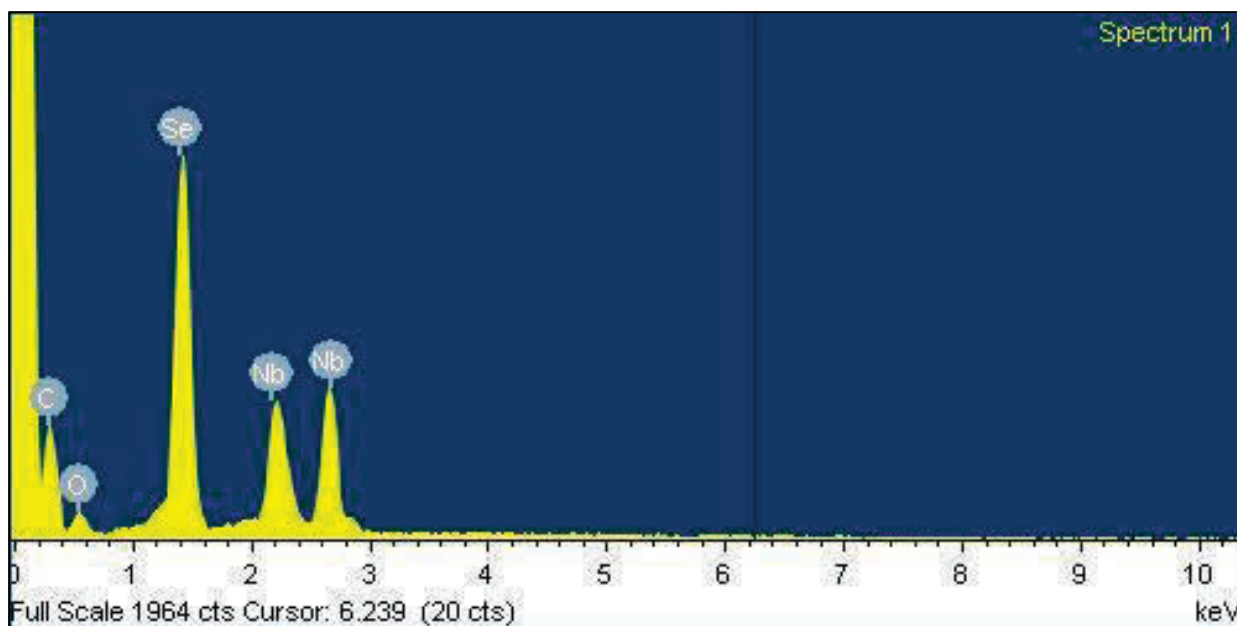


Figure 4.5: EDX spectrum of NbSe₂ particles synthesized using SU precursor.

The XPS survey spectrum of the as-synthesized nanoflowers shows the expected elemental compositions and the respective binding energies (**Figure 4.6**). The spectrum shows the presence of Nb, Se, C and O. The C is due to the capping agent and the O is as a result of the oxidation of the capping agent as well as the Nb₂O₅ observed in XRD. The % atomic composition shown in **Table 4.2** shows a high percentage of C, 85.3% attributed to the capping agent oleylamine. The percentage of O is relatively high and is attributed to both the oxidation of the capping agent as well as the formation of the metal oxide Nb₂O₅. The % atomic composition of both Nb and Se are relatively low and this might suggest that NbSe₂ nanoflowers readily oxidize on the surface to Nb₂O₅.

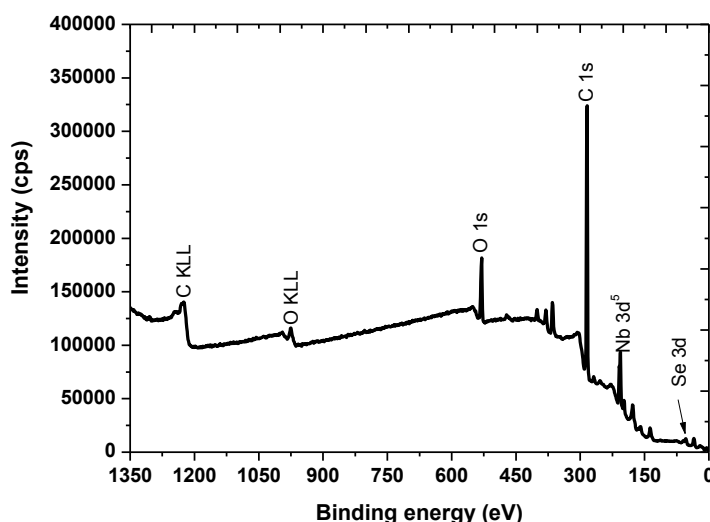


Figure 4.6: XPS survey spectrum of NbSe₂ particles synthesized using SU precursor.

The high resolution XPS spectra with the focus on C1s, O1s, Nb3d and Se3d were done to evaluate the surface in more details and the spectra are shown in **Figure 4.7**. The C1s core level spectrum shows the deconvoluted C-C peak attributed to the oleylamine, the C-O and O-C=O due to the oxidation of the capping agent. The O1s peak also shows the oxidation of the capping agent as well as Nb₂O₅. The Nb3d core level spectrum is characterized by three components, composed of the Nb⁴⁺3d_{5/2} (203.0 eV), the Nb⁵⁺3d_{5/2} (206.9 eV) and the Nb⁵⁺3d_{3/2} (209.3 eV). The Nb⁴⁺3d_{5/2} and the Nb⁴⁺3d_{3/2} peaks correspond to NbSe₂ while the Nb⁵⁺3d_{5/2} corresponds to Nb₂O₅. These results are consistent with work reported by Boscher *et al.* [27]. The Se3d core level spectrum shows two peaks all attributed to the NbSe₂.

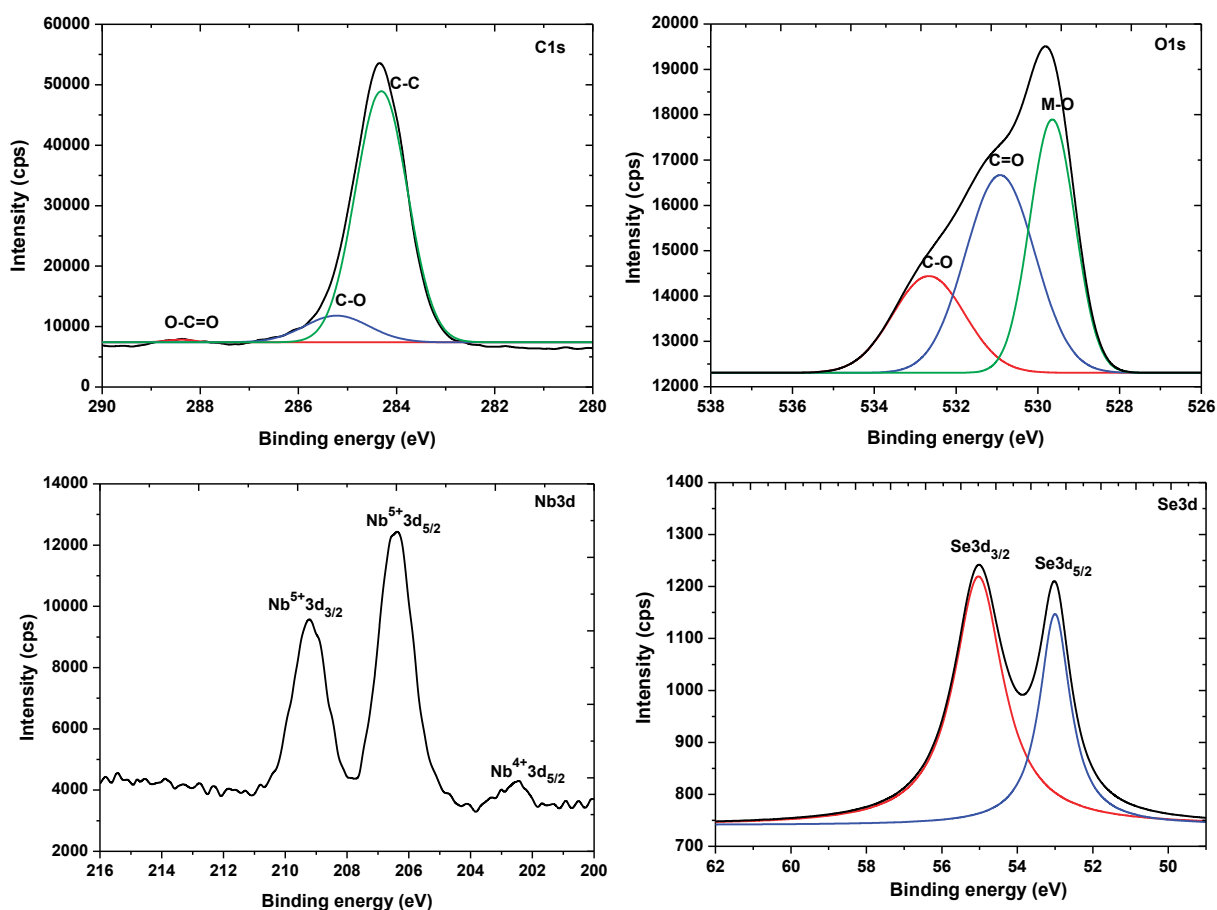


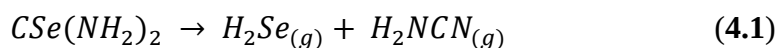
Figure 4.7: High resolution core level spectra of NbSe₂ particles synthesized using SU with focus on C1s, O1s, Nb3d and Se3d.

Table 4.2: Summary of the atomic composition stoichiometric assignments obtained from the fitting of the XPS spectra reported in Fig. 4.6 and 4.7

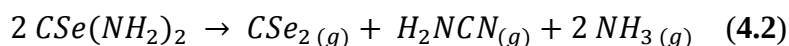
Element	Atomic %	Peak Binding energy (eV)	Assignments	Assignment %
C	85.3	284.8	C-C	78.6
		286.3	C-O	4.7
		288.8	O-C=O	1.9
O	10.2	530.2	M-O	5.4
		531.7	C=O	4.1
		533.3	C-O	2.4

Nb	2.9	203.0	Nb ⁴⁺ 3d _{5/2}	0.1
		206.9	Nb ⁵⁺ 3d _{5/2}	1.5
		209.3	Nb ⁵⁺ 3d _{3/2}	0.4
Se	1.5	53.4	Se3d _{5/2}	0.7
		55.5	Se3d _{3/2}	0.6

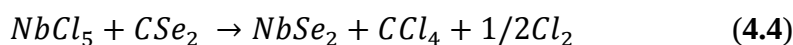
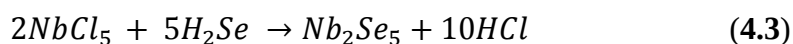
To further understand how the nanoflowers derived from SU form, aliquots were taken and the progression of the reaction was studied as in **Figure 4.8**. In the colloidal heat-up method, the decomposition of the precursors drives the formation of the nuclei. For selenourea derived particles, the proposed decomposition of selenourea is similar to that of thiourea and this then reacts with the metal salt to form the desired NbSe₂. Studies have been done to elucidate the thermal decomposition of thiourea. Theoretical studies suggest that there are almost eighteen reaction pathways that could take place during the thermal decomposition of thiourea [28-30]. Nevertheless, two pathways dominate:



or;



From these decomposition products, NbSe₂ can most likely form from the reaction with CSe₂ as H₂Se will yield another stoichiometry as shown in the equations below:



From the TEM images below, the nanoflowers are essentially formed from nanosheets. After 5 min there is a formation of flocculates which are the starting material. Savjani *et al.* reported that MoS₂ initially forms flocculates which are known to have lateral dimensions ranging from hundreds to thousands nanometers [31]. This is no surprise as NbSe₂ is a layered material and is known to have a similar structure to that of MoS₂. Guo *et al.* reported that the formation of nanosheets is due to low supersaturation which allows growth to occur in two directions [32]. After 30 min the flocculates are consumed forming ‘wrinkled’ and irregular nanosheets. After 45 min the flocculates are no longer observed because the nanosheets have rearranged

themselves and formed hierarchal nanosheets. Finally, after 120 min nanoflowers are formed by curled nanosheets.

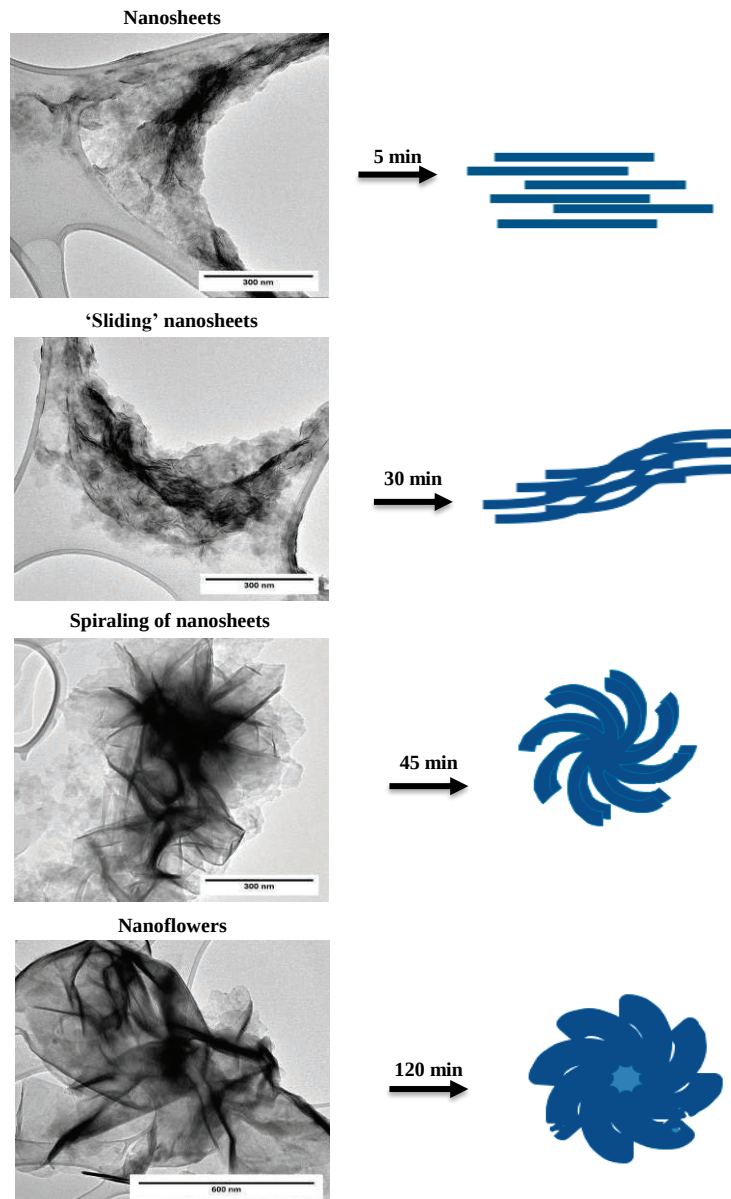


Figure 4.8: Mechanism for the evolution of the nanosheets in NbSe₂ particles synthesized using SU.

4.4 Conclusion

Three selenium precursors were used to synthesize NbSe₂ nanoflowers. The Se and SeO₂ precursors resulted in the 2H-NbSe₂ phase with significant Nb₂O₅ impurities. On the other hand, the SU precursor resulted in the formation of the 3R-NbSe₂ phase with minor impurities. The 2H-NbSe₂ and 3R-NbSe₂ showed semiconducting characteristics similar to other layered

2D materials with the band gaps ranging from 2.0 eV to 2.5 eV. The purest nanoflowers derived from SU, showed from the EDX and XPS that there was the presence of oxygen however from the XPS, it was seen that a significant amount was due to the oxidation of the capping agent oleylamine. By monitoring the particle growth over time using TEM, it was shown that the nanoflowers grow from flocculated nanosheets to hierarchal nanosheets and finally nanoflowers.

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Chapter 5

Synthesis of Nb₂Se₉ using selenium, selenium oxide and selenourea as selenium precursors

5.1 Introduction

So far, all reaction parameters have been investigated for the synthesis of niobium selenide nanomaterials (chapter 3). The effect of Se precursors has also been evaluated in chapter 4, where their reaction with NbCl₅ was evaluated. This study was performed to investigate the effect of Nb precursors on the nucleation and growth process of niobium selenide nanoparticles. The most important factor in colloidal synthesis is the choice of precursors [1]. The metal precursors are usually metal complexes which contain different types of ligands. Nucleation depends on the rate of monomer in flux, that is how quickly can the ligand bonds be broken to form the free monomer [2, 3]. The use of highly reactive precursors will cause an increase in the nucleation and growth rate which will result in lower yield of nanoparticles and size distribution [2]. On the other hand, the use of precursors with low reactivity will produce the same results by following a different pathway. Therefore, essentially a precursor with moderate reactivity is required because there will be a balance between nucleation and growth resulting in higher yield and narrow size distribution of nanoparticles [2]. Shankar *et al.* synthesised Cu nanoparticles using different metal salts such as Cu(CH₃COO)₂, CuCl₂ and CuSO₄ [4]. They discovered that the shape and size of the Cu nanoparticles were dependent on the type of Cu precursor used [4]. Mayekar *et al.* used three different metal salts to synthesise ZnO nanoparticles and obtained nanoflowers, rice-like and spherical nanoparticles when Zn(NO₃)₂, ZnCl₂, and ZnC₄H₆O₄ were used, respectively [5]. Arellano also made a comparative study on the use of Cd(CH₃COO)₂, CdCl₂ and Cd(NO₃)₂ to synthesise CdSe nanoparticles [6].

According to the HSAB theory, Nb⁴⁺ is a hard lewis acid and F⁻ is a harder lewis base compared to Cl⁻ [7]. Therefore, Nb⁴⁺ is likely to form a more stable complex with F⁻ than Cl⁻. As such, more energy will be required to decompose NbF₅ than NbCl₅. Moreover, according to the ionic-covalent theory hard acids tend to bind with hard bases through ionic forces [8]. Nb⁴⁺ has tightly held outer electrons and vacant orbitals available not too high in energy. These orbitals can accept electrons from the ligand such as F to form π bonds [9]. In addition to the theory, pentahalides have a diversity in their structure. For example, NbCl₅ has a dimer structure (i.e.

two Cl bridges) [10] whereas NbF_5 has a tetramer structure (i.e. four F bridges) within a single unit cell [11]. In a typical dimer there are $(\text{NbCl}_5)_2$ units, the bridge-bonds are longer and weak which causes the axial bonds to bend inward [11]. A tetramer structure contain $(\text{NbF}_5)_4$ units, each unit is connected by a F-bridge forming a square [12]. Therefore, the nucleation and growth process of nanoparticles will be affected. Herein, the effect of NbF_5 as a metal precursor will be evaluated and compared with the NbCl_5 results in Chapter 4.

5.2 Experimental

5.2.1 Chemicals

The same chemicals in Chapter 4 were used including niobium (V) fluoride 98% were obtained from Sigma Aldrich and used without further processing.

5.2.2 Colloidal synthesis of Nb_2Se_9 nanomaterials

The same procedure in Chapter 4 was followed here, except that the metal precursor in this case was NbF_5 .

5.2.3 Characterisation of the Nb_2Se_9 nanomaterials

The same characterisation techniques were used as in Chapter 4.

5.3 Results and discussion

Niobium fluoride was reacted with different selenium precursors to yield different results. XRD was used to investigate the structural properties and phases of the nanoparticles and the results are shown in **Figure 5.1**. The particles from all Se precursors are indexed to a Nb_2Se_9 triclinic phase (PDF 01-078-1383) nanoparticles. However, the intensities of the peaks are different as such the crystallinity differ. The peaks from Se and SeO_2 derived samples are more intense than the SU sample hence suggesting good crystallinity. The peak widths are much narrower for Se and SeO_2 than SU nanoparticles; therefore indicative of different sizes.

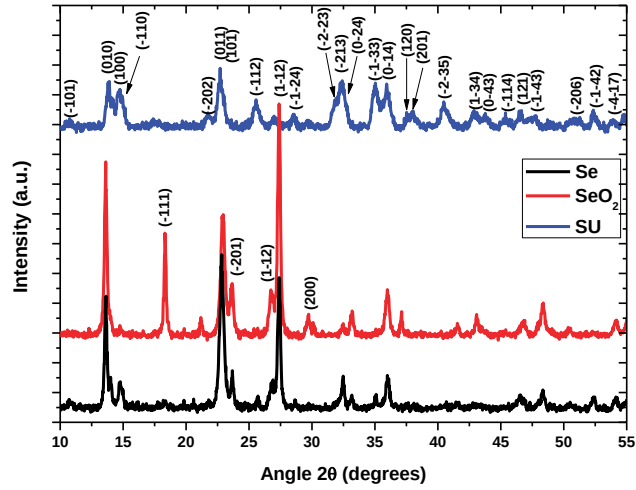
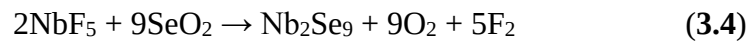
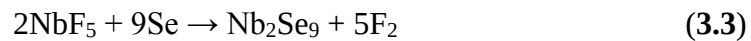
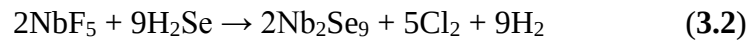


Figure 5.1: XRD patterns of Nb₂Se₉ nanoparticles formed from NbF₅ and various Se precursors.

The decomposition of SU has been proposed to undergo a two-step process in order to form selenium monomers to react with Nb for the formation of Nb₂Se₉. Firstly, the SU precursor undergoes decomposition and forms H₂Se and a carboamide (equation 3.1). Secondly, the H₂Se precursor undergoes an in-situ reduction to form the Se monomers (equation 3.2). On the other hand, the Se and SeO₂ precursors only undergo a single process which is reduction shown in equation 3.3 and 3.4, respectively. Therefore, the nucleation rate of Se and SeO₂ is faster than SU because the Se monomer can be obtained in a single step. Fast nucleation therefore results in more crystalline particles. In addition, for all samples, Nb₂Se₉ nanoparticles were formed when using the NbF₅ as a metal precursor whereas strictly NbSe₂ particles formed when the precursor was NbCl₅.



The morphologies of the nanoparticles were determined using TEM and SEM, shown in **Figure 5.2**. All the selenium precursors resulted in nanorods with different shapes and sizes. Chae *et al.* and Lee *et al.* reported that Nb₂Se₉ was a 1D material; therefore it is expected to crystallize in the form of nanorods [13, 14]. They obtained flat-nanorods that had broken ends [13]. The

Se derived nanorods are monodispersed than SeO_2 and SU nanorods with a length and width of $2.07 \pm 1.23 \mu\text{m}$ and $0.215 \pm 0.126 \mu\text{m}$, respectively. These nanorods are flat and have broken ends. SeO_2 and SU nanoparticles have a mixture of nanorods and nanoslabs. Therefore, each selenium precursor has an effect on the morphology.

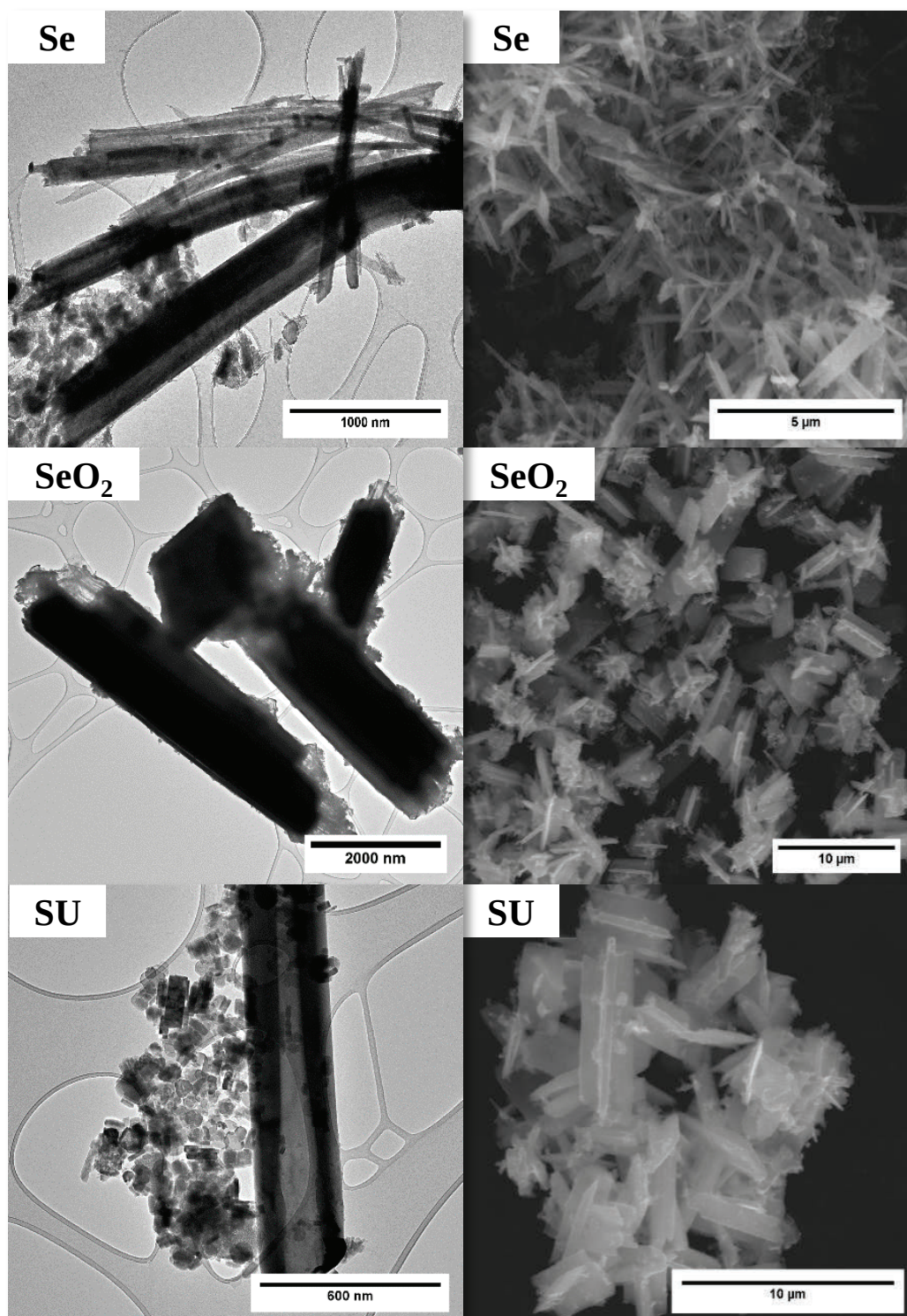


Figure 5.2: TEM (left side) and SEM (right side) images of Nb₂Se₉ nanoparticles formed from NbF₅ and various Se precursors.

The optical properties were analysed using UV-Vis spectroscopy and the results are shown in **Figure 5.3 (a)**. All selenium precursors resulted in peak-tailing in the absorption spectra. Peak-tailing is a result of polydispersity, which confirms the observation in the TEM and SEM images above (all nanoparticles were polydispersed irrespective of the type of Se precursor used). The Tauc plots are calculated to estimate the bandgap of the nanoparticles (**Figure 5.3 (b)**). The band gaps of Se, SeO₂ and SU derived particles are estimated to be 1.7 eV, 2.3 eV and 1.9 eV. The bandgaps are in the visible region of the spectrum and the Se derived particles' bandgap is the most red-shifted compared to the other two selenium precursors. The optical properties of NbF₅ derived particles are markedly different from the NbCl₅ derived particles reported in Chapter 4. The band gap values of NbCl₅ derived nanoparticles were approximately 2.5 eV, 2.4 eV and 2.1 eV for the corresponding selenium precursors. These are blue-shifted from the NbF₅ derived particles most likely due to different morphologies observed. The NbCl₅ derived nanoparticles were nanosheets.

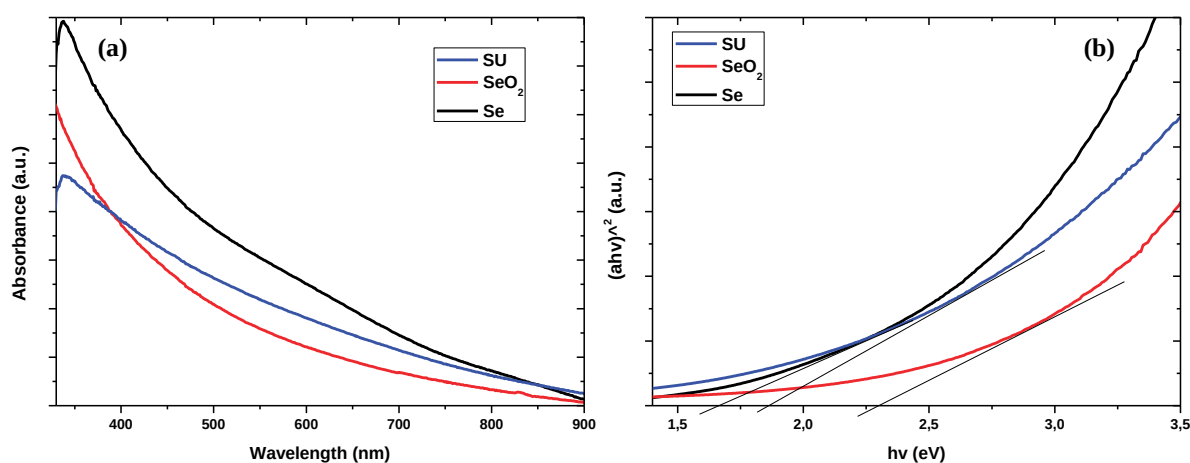


Figure 5.3: (a) UV-Vis absorption spectra of Nb₂Se₉ nanoparticles formed from NbF₅ and various Se precursors and (b) their corresponding Tauc plots.

The composition of Se derived nanoparticles was investigated further by the use of EDX. The EDX spectrum shown in **Figure 5.4** has the expected Se and Nb peaks but there is a presence

of a small O peak. Since this was not observed in the XRD pattern above, the assumption is that only the surface of the particles has been oxidised.

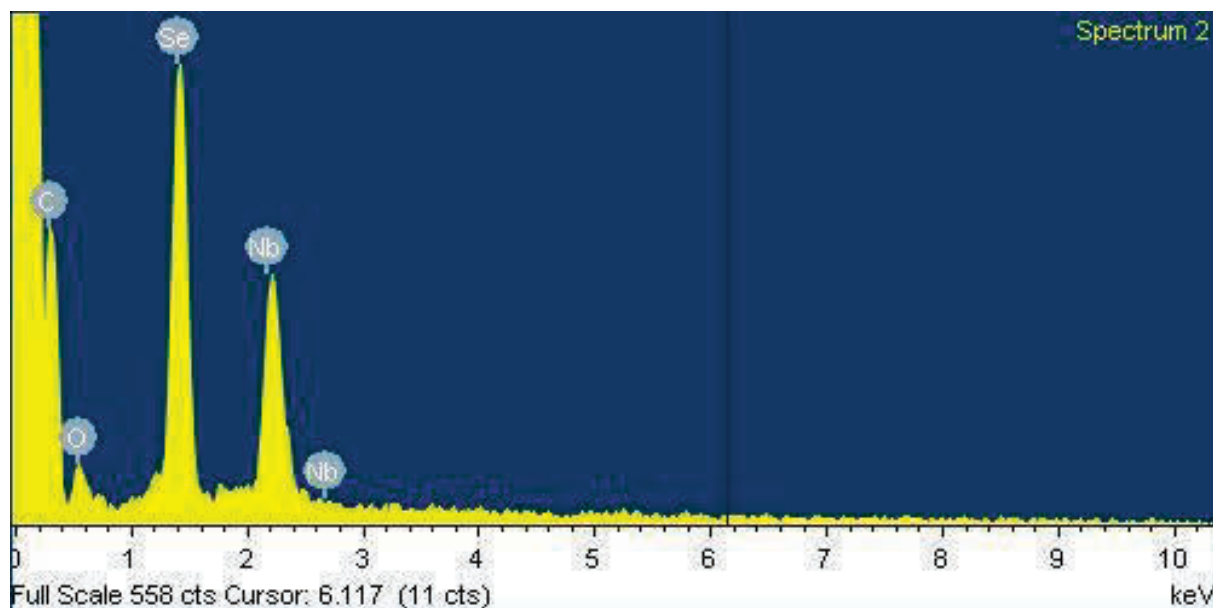


Figure 5.4: EDX spectrum of Nb_2Se_9 particles synthesized using Se precursor.

To further evaluate the composition, XPS was undertaken. The XPS survey spectrum of the Nb_2Se_9 showed the presence of Nb, Se, C and O (**Figure 5.5**). The C is attributed to the capping agent and the O is due to the oxidation of the capping agent as well as the Nb_2O_5 on the surface of the nanoparticles. This is in agreement with the observed EDX results. The % atomic composition shown in **Table 5.1** shows a high percentage of C, 77.9% attributed to the capping agent, OLA. The percentage of O is relatively high and is attributed to the oxidation of OLA as well as Nb_2O_5 . The % atomic composition of both Nb and Se are relatively low and this might be due to the oxidation on the surface of Nb_2Se_9 nanorods to Nb_2O_5 .

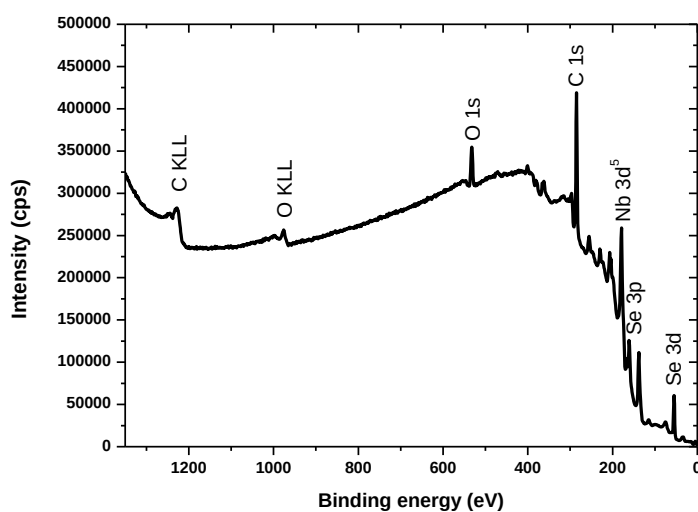


Figure 5.5: XPS survey spectrum of Nb₂Se₉ particles synthesized using SU precursor.

High resolution XPS was performed for further analysis of O1s, C1s, Se3d and Nb3d shown in **Figure 5.6**. The strong C1s peak is attributed to OLA and O1s is responsible for both the OLA and Nb₂O₅. The Nb3d core level spectrum has four peaks assigned to Nb⁴⁺3d_{5/2} (203.6 eV), Nb⁴⁺3d_{5/2} (206.3 eV), Nb⁵⁺3d_{5/2} (207.3 eV), and Nb⁵⁺3d_{5/2} (210.0 eV). The Nb⁴⁺3d_{5/2} and the Nb⁴⁺3d_{3/2} peaks correspond to Nb₂Se₉ while the Nb⁵⁺3d_{5/2} and Nb⁵⁺3d_{3/2} corresponds to Nb₂O₅.

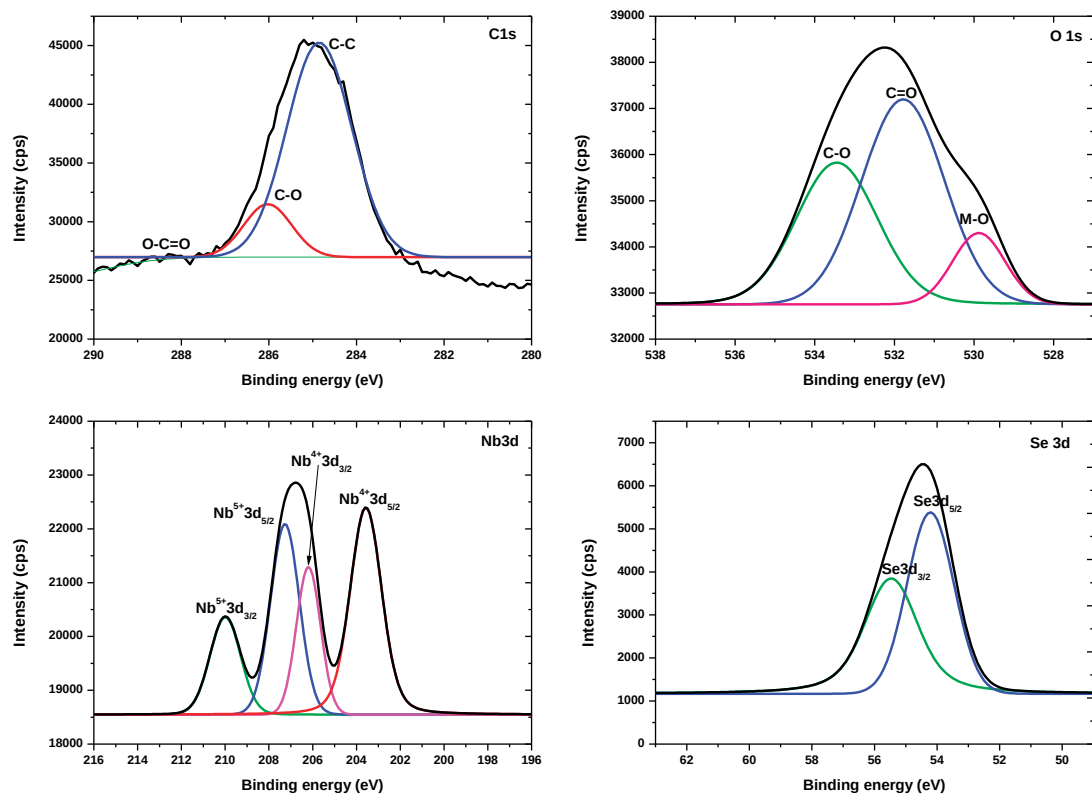


Figure 5.6: High resolution core level spectra of Nb₂Se₉ particles synthesized using Se with focus on C1s, O1s, Nb3d and Se3d.

Table 5.2: Summary of the atomic composition stoichiometric assignments obtained from the fitting of the XPS spectra reported in Fig. 5.6 and 5.7

Element	Atomic %	Peak Binding energy (eV)	Assignments	Assignment %
C	77.9	284.9	C-C	59.5
		286.2	C-O	6.0
		288.7	O-C=O	4.1
O	13.3	530.1	M-O	2.8
		531.8	C=O	5.5
		533.6	C-O	4.4
Nb	2.5	203.6	Nb ⁴⁺ 3d _{5/2}	1.6
		206.3	Nb ⁴⁺ 3d _{5/2}	1.6
		207.3	Nb ⁵⁺ 3d _{3/2}	1.3
		210.1	Nb ⁵⁺ 3d _{5/2}	1.6

Se	6.3	54.2	Se3d _{5/2}	8.3
		55.4	Se3d _{3/2}	3.7

The reactivity of NbF₅ with selenium precursors differs from NbCl₅ (evaluated in Chapter 4), because it favours the formation of triclinic phase Nb₂Se₉ nanorods over hexagonal or rhombohedral phase NbSe₂ nanoflowers under the same conditions. Therefore, the nucleation and growth processes are also affected by the Nb precursors. For nucleation to occur, the Nb precursors undergo decomposition to form free Nb atoms. NbF₅ has four bridges where the F atom forms a bridge between two Nb atoms in a single unit cell. Whereas, NbCl₅ only has two Cl-bridges. Therefore, more energy is required to decompose NbF₅ than NbCl₅ which means the rate of nucleation will be lower because the influx of monomers is low. Moreover, Zhang *et al.* reported that Nb₂Se₉ can be converted to NbSe₂ by longer reaction time and higher temperature treatment [15]. As such, if the synthesis with NbF₅ can be performed at higher temperature and reaction time it may have the potential to form NbSe₂.

5.4 Conclusion

Triclinic phase Nb₂Se₉ nanoparticles were synthesized with the use of three selenium precursors and NbF₅ as a metal source. However, their morphology and optical properties varied with the variation of selenium precursors. Se precursor produced more monodispersed nanorods and the smallest bandgap compared to SeO₂ and SU. Therefore, the purity of the nanorods were investigated further and found that the surface of the nanoparticles was oxidised to Nb₂O₅. Moreover, NbF₅ favoured the formation of Nb₂Se₉ and NbCl₅ favoured the formation of NbSe₂.

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Chapter 6

NbSe₂ and Nb₂Se₉ nanostructures as alternative to Pt electrodes in dye-sensitized solar cells

6.1 Introduction

Inorganic nanomaterials have been used in solar cells for different roles ranging from absorber-layers to buffer layers, to sensitising material in quantum dot sensitized solar cell and counter electrodes in dye sensitized solar cells (DSSCs) [1, 2]. This is due to their unique properties such as material diversity, abundance, low cost, high catalytic activity, and ease of modification [2]. In solar cell devices, these nanomaterials have shown to have the potential based on thin films or quantum dots [1, 3-10]. The fabrication of the thin films can be split into three broad areas: chemical vapour deposition (CVD), atomic deposition and solution processing [1, 5-10]. CVD involves the deposition of the precursor in gas phase onto a substrate leading to the growth of the material at high temperatures [1]. This method has been used by researchers to produce high-quality thin films [11-15] and has a wide range of suitable precursors to use, from individual components to single source precursors [1]. The atomic deposition involves depositing a layer of individual components then annealed in the presence of a chalcogenide [16-19]. The advantage of this method is that it provides precise thickness control at the monolayer level which is essential for optimising the performance of the device [1]. However, the disadvantage is that it sometimes requires the use of ultra-high vacuum, thus not suitable for large-scale production. Also at the laboratory level, the equipment is custom built which makes it difficult to obtain reproducible results from one instrument to another. Solution processing technique, used in this study, is a two-step process where the transition metal chalcogenide (TMC) is synthesised first then dissolved in a solvent to form an ink which is then processed into a thin film [20, 21]. Essentially, there are two ways of making the thin film after the ink has been formed namely, spin-coating and drop-casting. Spin-coating involves depositing a small puddle of ink onto the centre of the glass substrate and then spinning the substrate at high speed [24]. This allows the ink to spread throughout the surface of the substrate uniformly and the solvent to evaporate. The final thickness and properties of the film depend on the nature of the ink i.e. viscosity, drying rate of the solvent used to disperse the nanoparticles, percent solids, surface tension, etc. [24]. However, the drawback to spin-coating is that any minor changes in the parameters that define the spin process will result in completely different properties of the thin film [25]. Drop-casting on the other hand involves covering the

surface of the substrate with the ink and allowing the solvent to evaporate. The resultant thin film depends on the evaporation rate of the solvent. The method in which these thin films are fabricated plays a crucial role in how the materials will perform in a DSSC device.

For DSSC counter electrode, Pt has been the benchmark due to its good conductivity and superior catalytic activities towards the reduction of triiodide (I_3^-) to iodide (I^-). However, Pt is an expensive noble metal. Although Singh *et al.* have reported transition metal dichalcogenides (TMDCs) that have great potential for DSSC devices over Pt, their long-term stability is just as important [28]. Pt may have the highest electrocatalytic activity for the reduction of triiodide (I_3^-) to iodide (I^-), but it is poor when it comes to iodine-free redox couples such as Co^{2+}/Co^{3+} and T_2/T^-). Therefore current researches are focussed on finding alternatives to Pt. Earth-abundant 2D materials have been of interest due to their high optical transparency and high catalytic activity [28]. As such, they have been researched in the last decade in the form of thin films [29]. Liang *et al.* used ultrathin MoS_2 nanofilms as CEs in DSSCs where their cyclic voltammetry revealed that they possessed excellent catalytic activity towards the reduction of I_3^- [30]. Ibrahim and Guo *et al.* deposited the $NbSe_2$ nanoparticles after making an ink onto an FTO-glass substrate via spin-coating and airbrush-method which is similar to drop-casting with addition of compressed air, respectively [26, 27]. In both cases, $NbSe_2$ showed potential to be used as CEs in DSSCs as their electrocatalytic activity was comparable to that of Pt [26, 27]. Herein, triclinic Nb_2Se_9 nanorods and $NbSe_2$ nanoflowers were investigated as potential CE for DSSCs.

6.2 Experimental

6.2.1 Chemicals

99.9% Lithium iodide, 95% lithium perchlorate, 99.8% Iodine, 98% toluene, 99.9% acetonitrile were purchased and used without any further purification.

6.2.2 Fabrication of the CE thin-film

The nanoparticles were dissolved in toluene and the mixture was sonicated for 30 min to form an ink. The FTO-glass substrate was cleaned with soap-water and sonicated for 15 min. The slides were rinsed with distilled water and sonicated further for another 15min and lastly with isopropanol and sonicated for 15 min. The slides were left to dry before the ink was deposited onto them. Two methods for depositing the ink were used:

- (i) Drop-cast: the ink was drop-casted onto a clean FTO-glass slide and left to dry at room temperature. The thin film was baked for 60 min at 120 °C in an oven.
- (ii) Spin-coat: the ink was deposited onto the substrate and a spin-coater CHEMAT technology KW-4A was used to spread the ink uniformly. The thin film was baked for 60 min at 120 °C in an oven.

The Pt-CE was formed by sputter-coating three coats of Pt onto a clean FTO-glass slide.

6.2.3 Electrocatalytic activity

Cyclic voltammetry (Metrohm 728 stirrer with the GPES software) was used to analyse the CEs. A three-electrode system was used where the as-prepared NbSe_2 -CE acted as the working electrode, a Pt wire acted as the counter electrode and an Ag/AgCl electrode acted as the reference electrode (**Figure 6.1**). The electrolyte contained an anhydrous acetonitrile solution of 49 mM LiClO_4 , 50 mM LiI and 9.85 mM I_2 . The electrolyte was purged for 300 s before scanning using a scan rate of 50 mV.

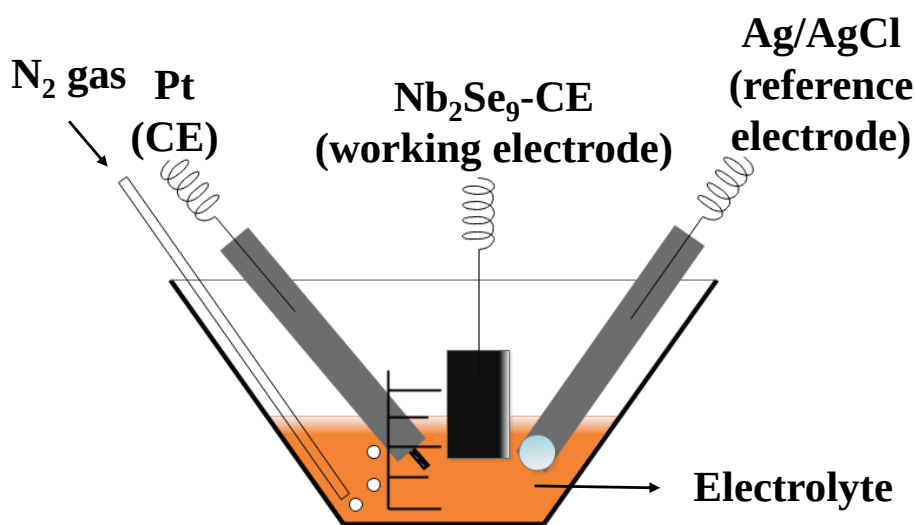


Figure 6.1: Cyclic voltammetry set-up.

6.3 Results and discussion

The electrocatalytic activity of the CEs was determined by cyclic voltammetry (CV), where the scan rate was varied to investigate the effect of the scan rate on the current density of each CE. Based on equation 6.1, there exist a relationship between the current density and square root of the scan rate. As such, an increase in scan rate causes the diffusion layer thickness to decrease and the electrochemical polarisation to increase which results in high overpotential and poor reversibility [2].

$$i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} V^{1/2} C \quad (6.1)$$

Where i_p is the peak current density, n is the number of electrons transferred, A is the area of the electrode, D is the diffusion coefficient, V is the scan rate, and C is the concentration [2]. The scan rates were 10, 20, 50 and 100 mV/s, where up to five scans were performed to also investigate the stability and reproducibility of the CEs. Typically, there are two pairs of redox peaks where the left pair is due to the reduction of I_3^- and the right pair is due to the oxidation of I^- . The Pt-CE, shown in **Figure 6.2**, is stable and reproducible irrespective of the scan rate used because the scans remained unchanged for each scan rate. However, current density decreased with a decrease in scan rate from 10 mV/s to 100 mV/s causing the peaks to be less defined. The cathodic peaks appear at 0.36 V and 0.50 V. The performance of the DSSC depends on the reduction whereas as the oxidation does not have that much effect [31]. Ibrahim *et al.* reported that in general, the higher the cathodic current peak the better the catalytic capability of the CE towards the reduction of I_3^- to I^- in DSSCs [26].

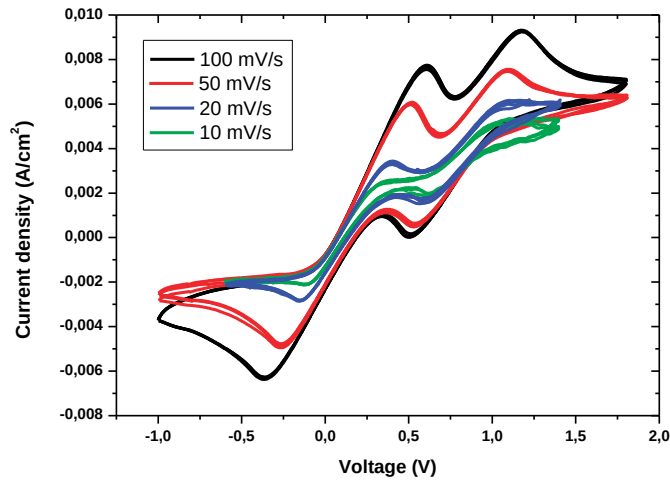


Figure 6.2: Cyclic voltammograms of the Pt-CEs at various scan rates after 5 scans.

The morphology of the nanomaterials used in this study are shown in **Figure 6.3**. Two methods were used to fabricate the niobium selenide CEs i.e. spin-coat and drop-cast. **Figure 6.4** shows the cyclic voltammograms of NbSe₂ nanoflowers at different scan rates (10 mV/s, 20 mV/s, 50 mV/s, and 100 mV/s). The current densities increase with an increase in scan rate. The drop-casted CE has a lower current density compared to the spin-coated CE, with the value of 0.0087 A/cm² and 0.0090 A/cm² at a scan rate of 100 mV/s. Both CEs are stable and reproducible irrespective of the scan rate. Moreover, the drop-casted CE cathodic peaks are not as defined

as those of the spin-coated CE. Therefore, the spin-coated CE has the better catalytic capability for the reduction of I_3^- to I^- .

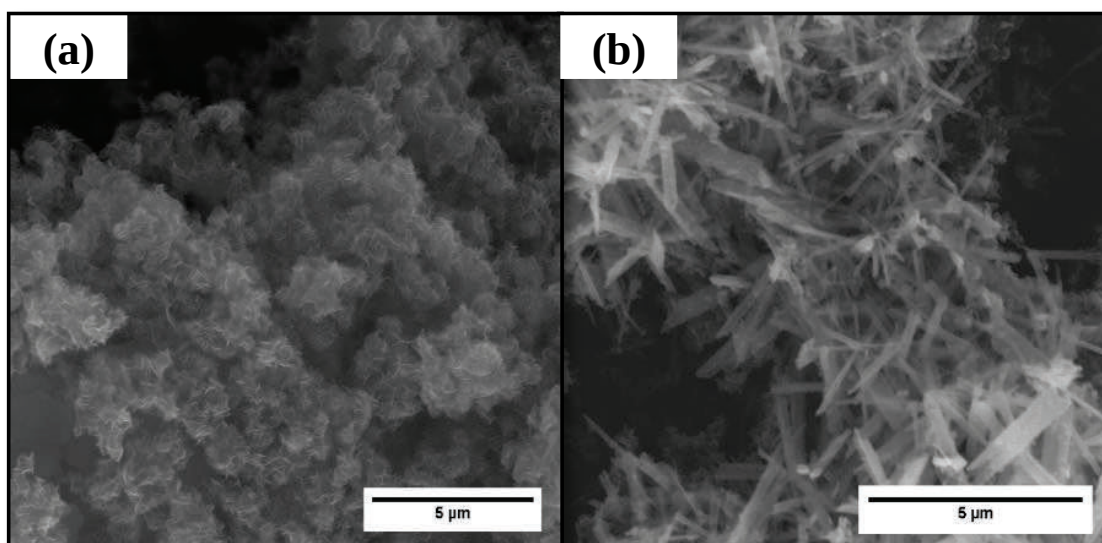


Figure 6.3: SEM images of (a) NbSe₂ nanoflowers and (b) Nb₂Se₉ nanorods.

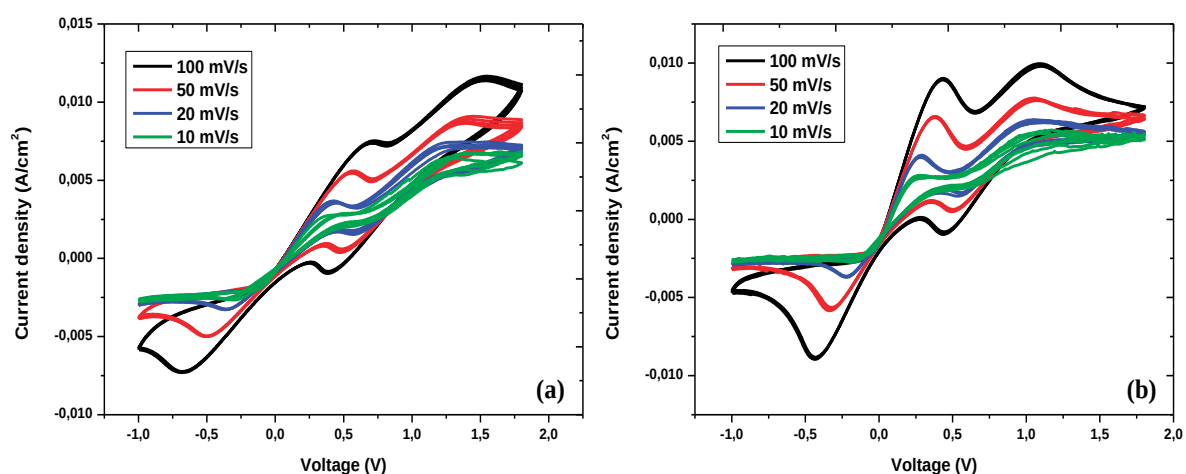


Figure 6.4: Cyclic voltammograms of the NbSe₂-CEs at various scan rates after 5 scans; (a) drop-casted and (b) spin-coated.

The Nb₂Se₉ CE was also analysed, and the spin-coated CE seems to have a better capability of reducing I_3^- to I^- than the drop-casted CE shown in **Figure 6.5**. However, the drop-casted CE is stable but at 100 mV/s it has a lower current density as well as a different electrocatalytic activity than the rest of the scan rates (**Figure 6.5 (a)**). The spin-coated CE is not stable at scan rates of 100 mV/s and 20 mV/s, because the scans are different (**Figure 6.5 (b)**). Therefore, the

Nb_2Se_9 spin-coated CE produces the desired results at 50 mV/s because it has the highest current density.

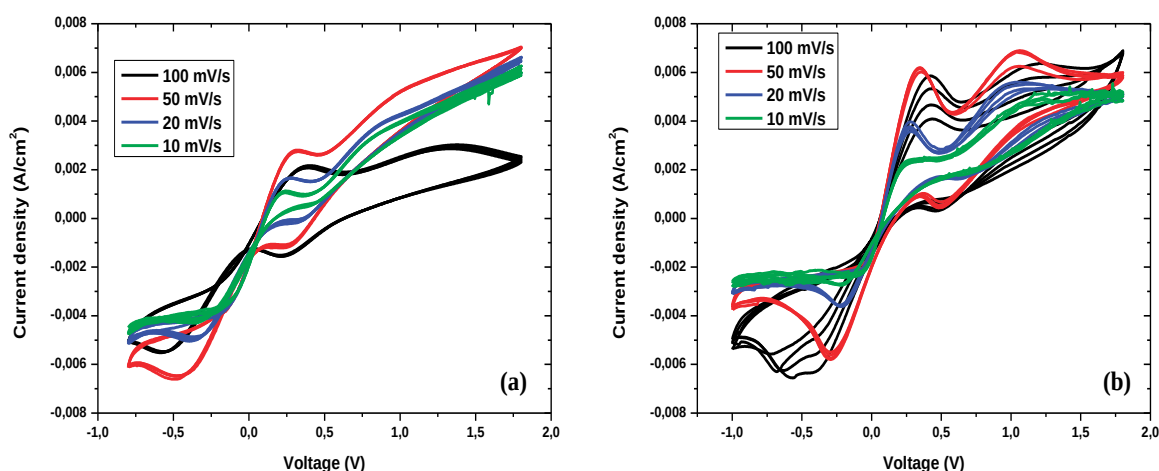


Figure 6.5: Cyclic voltammograms of the Nb_2Se_9 -CEs at various scan rates after 5 scans; (a) drop-casted and (b) spin-coated.

As proof of principle and to highlight the possibility of using niobium selenide CEs as alternatives to the Pt-CE, the two CEs (spin-coted: NbSe_2 and Nb_2Se_9) were compared with the Pt-CE. The cyclic voltammograms are shown in **Figure 6.6 (a)**, indicates that both Nb_2Se_9 and NbSe_2 CEs have the potential to be used in DSSCs because their electrocatalytic activities are comparable to that of Pt since the peak positions are similar. They also have a higher current density than the Pt-CE. However, there is a slight shift to the negative voltage of one of the cathodic peaks. The peak-to-peak separation (E_{pp}) is also an important parameter to look at when comparing the catalytic activity of electrodes [32]. The cathodic peak represents the reduction velocity and the E_{pp} is associated with the reversibility of the redox reaction [32]. The Pt-CE has an E_{pp} of 805 mV whereas NbSe_2 and Nb_2Se_9 CEs are 819 and 762 mV, respectively. Therefore, the Nb_2Se_9 -CE has better reversibility and electrocatalytic activity because it has a smaller E_{pp} than the Pt-CE. However, the NbSe_2 -CE has a similar E_{pp} as the Pt-CE. Moreover, the NbSe_2 -CE exhibited the highest current density compared to Nb_2Se_9 -CE which is an indication of better electrocatalytic activity. As such, of the two niobium selenide materials NbSe_2 is a better CE than Nb_2Se_9 because of its stability, comparable E_{pp} and higher current density than that of Pt. This is due to the fact that the NbSe_2 nanoflowers which are essentially nanosheets that are ‘crumbled up’ have the largest surface area and better coverage of the FTO-glass substrate than the Nb_2Se_9 nanorods [26]. Therefore, spin-coating the

nanoflowers onto the FTO-glass substrate is an effective way to increase the active surface area of the CEs as well as enhancing their electrocatalytic ability [26].

Ibrahim *et al.* compared NbSe₂ nanosheets and nanorods CEs with the Pt-CE and reported that the nanosheets exhibited better electrocatalytic activity than the nanorods [26]. They also reported that the nanosheets film performed better because the nanosheets sample exhibited intercrossed nanosheet conglomeration whereas the nanorods sample was made up of irregular nanorod structures [26]. Guo *et al.* also obtained the same results with NbSe₂ nanosheets compared to nanorods. **Figure 6.6 (b)** shows the relationship between the current density and square root of the scan rate and the observation is in good agreement with equation 6.1 [2]. The electrochemical double layer capacitance of spin-NbSe₂ is much larger than the Pt-CE, therefore it has a greater effective surface area. The effective surface area is an important factor for the estimation of the catalytic activity [30]. This is expected to be linearly proportional to the electrochemical double layer capacitance [2, 30]. The same outcome was obtained by Liang *et al.* with a MoS₂-based CE [30], hence it is no surprise because MoS₂ has a similar structure to NbSe₂.

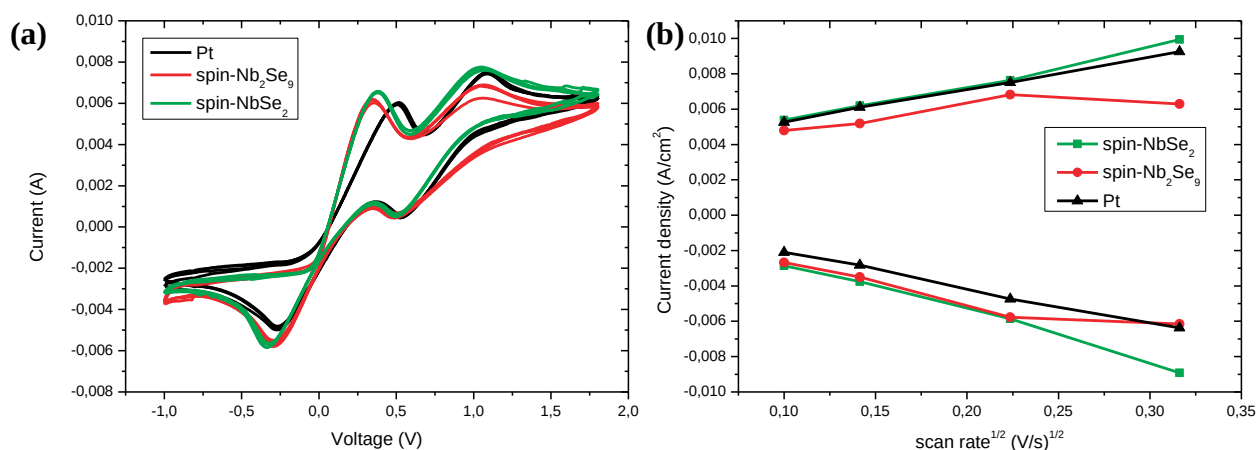


Figure 6.6: (a) Cyclic voltammograms with the comparison of Pt-CE with the Nb₂Se₉ and NbSe₂ CEs, (b) Linear fitting of the capacitive current densities of Pt compared with the Nb₂Se₉ and NbSe₂ CEs.

Table 6.1: Summary of the current density and peak-to-peak separation (E_{pp}) of each CE analyzed

CE	Current density (mA/cm ²)	E_{pp} (mV)
Pt	4.86	805
Spin-NbSe ₂	5.88	819
Spin-Nb ₂ Se ₉	5.66	762

6.4 Conclusion

In conclusion, two methods were used to successfully fabricate niobium selenide CEs. The effectiveness of each method was evaluated by cyclic voltammetry, and we found that the spin-coat method produced stable and reproducible CEs with defined peaks than the drop-cast method. The spin-coated NbSe₂-CE was more stable and reproducible than the spin-coated Nb₂Se₉-CE. When these two CEs were compared to that of Pt, the NbSe₂-CE showed the highest electrocatalytic activity compared to Nb₂Se₉ and Pt CEs. Such results indicate that the NbSe₂ nanoflowers could provide cost-effective CEs alternative to the noble metal Pt in DSSCs because of their high surface area and coverage.

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Chapter 7

Overall conclusions and recommendations

7.1 Conclusions

In this dissertation, the colloidal synthesis method was explored in synthesizing niobium selenide nanoparticles. The effect of the reaction parameters (reaction time, temperature, precursor concentration, capping agents, and Nb and Se precursor) was investigated. NbSe₂ nanoflowers were successfully synthesised at 320 °C for 120 min in OLA with a concentration of 0.125 M using NbCl₅ as a metal precursor. The use of SU produced rhombohedral NbSe₂ nanoflowers whereas Se and SeO₂ produced the hexagonal phase. As such, the optical properties were also affected. The SU nanoflowers had less Nb₂O₅ on the surface and were investigated further for application in DSSCs. However, Nb₂Se₉ nanorods were favoured at temperature below 320 °C, shorter reaction time, higher concentration of the Nb and Se precursors (0.500 M), the use of shorter chained capping agents (HDA and ODE) and NbF₅ as a metal precursor. The Se nanorods were more crystalline and monodispersed than the SU and SeO₂ nanorods, hence they were chosen for the application in DSSCs. The use of different capping agents resulted in different morphologies and size distribution because the capping agents were capped onto the surface of the nanoparticles through their terminal functional groups.

The electrochemical properties of these materials were investigated by CV. Each niobium selenide CE was fabricated using the spin-coating and drop-casting method. These CEs were compared with a sputter-coated Pt-CE. We found that the NbSe₂-CE has the potential to replace Pt-CEs because of its higher current density, larger electrochemical double layer capacitance and comparable E_{pp} to Pt. Such results indicate that NbSe₂ nanoflowers have the potential to provide cost-effective CEs because of high surface area and coverage. The Nb₂Se₉-CE was comparable to the Pt-CE but it was not stable. In addition, the synthesis method can also lower the cost due to the use of low temperatures, low reaction time, and ease of usage.

7.2 Recommendations

- To control morphology and obtain a narrow size distribution, the hot-injection colloidal synthesis method should be attempted.

- To further investigate the capping agents, use of DOSY (diffusion ordered) and NOE (nuclear overhauser effect) spectroscopy.
- To use NbF_5 in longer reaction times or even higher temperatures with the attempt to convert Nb_2Se_9 into NbSe_2 .
- Explore other Nb precursors, such as $\text{Nb}(\text{OCH}_2\text{CH}_3)_2$ for the synthesis of niobium selenide nanoparticles.
- Evaluate other methods that can be used to fabricate thin films that can reproduce the same thin films.
- Fabricate the DSSC device and further investigate the potential used of niobium selenide nanoparticles.