

Tailored synthesis of shaped carbon nanomaterials over supported Au, Ni, La and La-Ni on novel radially aligned nanorutile: Characterisation and investigation of properties



Farai Dziike Mutambara

School of Chemistry

Molecular Sciences Institute

University of Witwatersrand

This thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

Declarations

I declare that this thesis is my own unaided work. It is being submitted for the Degree of Doctor of Philosophy in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

Signature of Candidate

_____ on the _____ day of _____ 2017

Contents

Tailored synthesis of shaped carbon nanomaterials over supported Au, Ni, La and La-Ni on novel radially aligned nanorutile: Characterisation and investigation of properties

.....	i
Declarations	i
Contents	ii
Acknowledgments.....	viii
Abstract.....	1
List of Abbreviations	5
Conference presentation.....	7
Chapter 1.....	9
1.1 Introduction.....	9
1.2 Aim and Objectives.....	12
1.2.1 Aim	12
1.2.2 Objectives	12
1.3 Research Justification	13
1.4 Scope of the Research.....	13
References.....	14
2.1 Literature review.....	16
2.1.1 Titanium dioxide (TiO ₂).....	16
2.1.2 Lanthanum (La) as a catalyst	19
2.1.3 Nickel (Ni) as a catalyst	19
2.1.4 Gold (Au) as a catalyst.....	19
2.1.5 Lanthanum-Nickel (La-Ni) co-loaded on RANR	23
2.2 Deposition-precipitation (DP) methods.	24
2.3 Synthesis of carbon nanomaterials.....	25
2.4 Photocatalysis studies	29
References.....	30
Chapter 3.....	37
3.1 Methodology.....	37

3.1.1	Preparation of radially aligned nanorutile.....	37
3.1.2	Loading of metal catalysts on radially aligned nanorutile support	37
3.1.3	Deposition-precipitation method using urea (DPU).....	37
3.1.4	Chemical vapour deposition synthesis of carbon nanomaterials	38
3.1.5	Characterisation of RANR and supported catalysts.....	39
3.2	Analyses.....	39
3.2.1	Powder X-ray diffraction (PXRD).....	40
3.2.2	Electron probe microanalysis (EPMA)	42
3.2.3	Scanning electron microscopy (SEM)	43
3.2.4	Transmission electron microscopy (TEM).....	44
3.2.5	Energy dispersive X-ray spectroscopy (EDS).....	46
3.2.6	Temperature programmed reduction/oxidation (TPR/TPO)	47
3.2.7	BET surface area analysis (BET).....	48
3.2.8	Fourier transform infra-red (FTIR) spectroscopy	49
3.2.9	Laser Raman spectroscopy.....	50
3.2.10	Thermogravimetric analysis (TGA).....	51
3.2.11	Ultraviolet–visible spectroscopy (UV-vis)	52
3.2.12	Solar simulator.....	53
	References.....	55
	Chapter 4.....	58
	Au, Ni and La metal nanoparticles supported on RANR.....	58
4.1	Introduction.....	58
4.2	Literature review	59
4.3	Experimental.....	61
4.3.1	Preparation of RANR.....	61
4.3.2	Deposition-precipitation method using urea (DPU).....	61
4.3.3	Characterisation techniques	62
4.4	Results and discussion	63
4.4.1	Structure and morphology of RANR	63
4.4.2	DPU of Au, Ni and La on RANR support	66
4.4.3	PXRD analysis	73
4.4.4	EDS analysis of the supported catalysts.....	75

4.4.5	BET surface area measurements	77
4.4.6	TPR analysis of supported catalysts.....	78
4.5	Conclusions.....	81
	References.....	82
	Chapter 5.....	86
	Synthesis of carbon nanofibers over supported lanthanum nanoparticle metal catalysts on RANR: A parametric study.....	86
5.1	Introduction.....	86
5.2	Literature review	87
5.3	Experimental.....	88
5.3.1	Preparation of La supported catalysts	88
5.3.2	Synthesis of CNFs.....	88
5.3.3	Characterisation of catalysts and carbon products	89
5.4	Results and discussion	89
5.4.1	PXRD analysis	89
5.4.2	Transmission and scanning electron microscopy.....	91
5.4.3	Percentage weight loading variation	97
5.4.4	Gas Flow rates.....	102
5.4.5	Reaction duration	102
5.4.6	Laser Raman spectroscopy (LRS).....	103
5.4.7	Thermogravimetric analysis (TGA).....	106
5.5	Conclusions.....	108
	References.....	109
	Chapter 6.....	112
	Synthesis of twisted carbon nanofibers over nickel decorated RANR	112
6.1	Introduction.....	113
6.1	Literature review	113
6.2	Experimental procedures	115
6.2.1	Preparation of the catalyst.....	115
6.2.2	Synthesis of twisted CNFs	116
6.2.3	Characterisation of catalysts and CNFs	116

6.3	Results and discussion	117
6.3.1	Effect of RANR support on Ni in the Ni/RANR catalyst	117
6.3.2	Effect of time	122
6.3.3	Effect of Ni loading.....	130
6.4.4.	Influence of flow rate on CNF formation	133
6.4	Conclusions.....	136
	References.....	137
	Chapter 7	140
	AuNPs supported on RANR for the synthesis of carbon nanomaterials	140
7.1	Introduction.....	140
7.2	Literature Review.....	141
7.3	Experimental.....	143
7.3.1	Preparation of supported Au catalysts.....	143
7.3.2	Synthesis of CNFs.....	143
7.3.3	Characterisation of catalysts and carbon products.	143
7.4	Results and discussion	144
7.4.1	PXRD and EPMA analysis	144
7.4.2	Transmission and scanning electron microscopy.....	147
7.4.3	CVD synthesis of Au/RANR catalysed SCNMs	150
7.4.4	Percentage weight loading	153
7.4.5	Gas flow rates and time variation	160
7.4.6	LRS	162
7.4.7	Thermogravimetric analysis (TGA).....	164
7.5	Conclusions.....	166
	Chapter 8.....	170
	Chemical vapour deposition synthesis of carbon nanomaterials over lanthanum-nickel mixed-metal catalyst supported on novel RANR.....	170
8.1	Introduction.....	170
8.2	Literature Review	171
8.3	Experimental	173
8.3.1	Preparation of supported La-Ni/RANR co-loaded catalysts.....	173

8.3.2	Synthesis of CNFs.....	173
8.3.3	Characterisation of catalysts and carbon products.	174
8.4	Results and discussion	174
8.4.1	PXRD and EPMA analysis.....	175
8.4.2	Temperature programmed reduction (TPR).....	178
8.4.3	Transmission and Scanning Electron Microscopy.....	180
8.4.4	Percentage weight loading.....	188
8.4.5	Effect of temperature on CNFs synthesis over La-Ni/RANR	188
8.4.6	Gas flow rates and time variation.....	189
8.4.7	LRS analysis of CNFs synthesised over La-Ni/RANR.....	190
8.4.8	Thermogravimetric analysis (TGA)	192
8.5	Conclusions.....	194
	References.....	195
	Chapter 9.....	199
	Influence of nickel, gold and lanthanum metal nanoparticles on the photocatalytic performance of RANR.....	199
9.1	Introduction.....	199
9.2	Literature Review.....	200
9.3	Experimental.....	201
9.3.1	Photocatalytic degradation of methyl orange (MeO).....	201
9.4	Results and discussion	202
9.4.1	UV–vis diffuse reflectance spectra (DRS).....	202
9.4.2	Photoluminescence (PL) analysis	204
9.4.3	Photodegradation rate studies	205
9.5	Conclusion	208
	References.....	209
	Chapter 10.....	213
	General Conclusions and Future Studies	213
10.1	Conclusions.....	213
10.2	Future Research	216
	Appendix A.....	217

Appendix B	227
Appendix C	232
Appendix D	238
Appendix E	246

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Abstract

Radially aligned nanorutile (RANR), in the form of microspheres, were synthesised using a hydrothermal method. Parameters such as reaction time, reaction temperature, reactant concentrations, as well as the solution's pH value result in RANR at various stages of formation. These consisted of densely packed and spherically aligned rutile phase nanorods which were oriented on a common crystallographic axis (110) that had independent terminating ends. The average diameter of these nanorods was between 2–12 nm, while their lengths ranged from 50–650 nm. Loadings ranging from 0.5 to 10 wt. % of metal nanoparticles of: Au, Ni, La and La-Ni onto the RANR support were achieved by using a deposition-precipitation method with urea. The choice of the metals was carefully done considering their positions on the periodic table. Ni is known to catalyse the synthesis of CNMs. Its behaviour was tested on the unique RANR support and compared to a higher transition metal, Au. Further testing was taken to a different metal group, La and effect of co-loading tested on La-Ni lanthanide-transition system. These metal nanoparticles (i.e. Au, Ni, La and La-Ni) that were deposited on RANR support were found to range in size from 2–3 nm, 1–6 nm, 2–8 nm and 2–10 nm respectively.

The PXRD pattern of the supported catalysts predominantly exhibited peaks of pure rutile with a major peak at 2θ value of 32.5° for the major rutile peak, and minor peaks at 42.5 , 48 , 52.1 , 64.0 , 66.5 , 75.0 and 82° respectively. La showed major peaks occurring at 2θ values of 30° and 15° with minor peaks at 26.5° and 28.0° . Ni had peaks at 2θ values 28° , 38.5° , 58° and 76° . Au had peaks occurring at 2θ values 24.3° , 28° , 43.5° and 48° . The peak positions of both La and Ni occurred at their respective 2θ values in the co-loaded La-Ni/RANR catalysts. TPR analyses revealed different reduction temperatures that increased with increase in wt. % loading. Au, Ni and La had mean reduction temperatures of 90°C , 500°C and 600°C respectively. However, the co-loaded La-Ni/RANR catalyst showed different reduction temperatures ranging $500 - 700^\circ\text{C}$ for loading of 1 – 10 wt. %. BET surface area analysis showed the Metal/RANR catalyst decreased from 50 to $33\text{ m}^2\text{ g}^{-1}$ with increase in wt. % loading from 5 – 10 wt. %. This implied that the metal particles were occupying the pore sited on the surface of the RANR support thereby decreasing the BET surface of the Metal/RANR catalyst with increase in metal wt. % loading.

Parametric studies for the synthesis of shaped carbon nanomaterials (SCNMs), in particular carbon nanofibers (CNFs), via chemical vapour deposition (CVD) using La, Au, Ni and co-

loaded La-Ni nanoparticles supported on RANR were performed under varying conditions including: wt. % loadings, temperature, flow rate, time and the type of metal used. The synthesis of CNFs from the decomposition of acetylene and hydrogen (H_2/C_2H_2) was targeted for the tailored synthesis of shaped carbon nanomaterials over supported Au, Ni, La and La-Ni on novel radially aligned nanorutile. Characterisation of the various metal/RANR catalysts and the CVD products was performed by: transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS), scanning electron microscopy (SEM), powder X-ray diffraction spectroscopy (PXRD), electron probe microanalysis (EPMA), laser Raman spectroscopy (LRS), thermogravimetric analysis (TGA), ultraviolet–visible spectroscopy (UV-Vis), Fourier transform infra-red spectroscopy (FTIR) and Brunauer-Emmett-Teller (BET) surface area measurements.

La/RANR supported the synthesis of straight chain CNFs. The CNFs grew predominantly from the tips of the La nanoparticles in the catalyst. The La nanoparticles were observed on most of the tips of the CNFs suggesting that tip-growth was the mechanism of growth of the CNFs synthesised over La/RANR. During CNFs growth, the La nanoparticles were displaced from their positions on the RANR support. The dislodged La nanoparticles had a tendency of undergoing sintering to form large sized nanoparticles. Consequently, the sintered La nanoparticles catalysed the synthesis of thick CNFs with diameters ranging from 40–270 nm as compared to supported La nanoparticles with an average particle size of 6 nm. It was observed that the morphology of the La metal nanoparticles played a critical role in the control of the morphology of the CNFs and is closely related to the properties of the metal particles, the reaction conditions and the pre-treatment of the La/RANR catalyst. At 5 wt. % loadings, the average diameter of the CNFs synthesized by the La/RANR catalysts was 40 nm while the lengths ranged from 200 nm – 100 μ m. Thus increased La wt. % loadings resulted in larger catalyst particle sizes which in turn caused larger fiber thicknesses.

The RANR was observed to be an actively interactive support that enhances the catalytic performance of the metal nanoparticles on its surface especially with Ni in the synthesis of CNFs over Ni/RANR catalysts. Variation of parametric conditions such as: wt. % loading, reaction temperature, gas flow-rate and reaction time had a significant effect on the morphology, mechanical properties and density of the CNFs grown on the Ni/RANR catalysts. The Ni/RANR catalysts were observed to support the synthesis of twisted CNFs in contrast to the straight chain CNFs synthesised on La/RANR catalysts. The twisted CNFs were synthesized by way of regular oriental nucleation of heptagons and pentagons along the

nanofibre body. CNFs growth time was found to be a crucial parameter that can be used to understand the growth process and tailor the artificial properties of the resulting carbon material assembly. There was a threshold time interval over which both growth of fibres was consistent and uniform coverage was achieved. Detailed studies on CNFs synthesised over 1, 8 and 10 wt. % Ni/RANR showed similar trends with time at various temperatures, wt. % loading and flow rates while the 0.5 wt. % Ni/RANR did not catalyse the synthesis of twisted CNFs except a few amorphous carbon deposited on the catalysts. It was also proved that the longer the time, the more graphitic the CNFs. Thus the carbon crystallisation on the Ni/RANR catalyst resulted in the formation of primary amorphous carbon. Then sufficient time of heating transformed the carbon into graphitic material while the catalyst shaped it into its specific twisted morphology.

Gold however, presented a different set of trends in its performance as a catalyst supported on RANR. The CVD products which formed over Au/RANR catalysts were observed to vary under different parametric reaction conditions. At low wt. % loading, catalysts catalysed the formation of amorphous carbon material. However, Au/RANR at higher wt. % loading was observed to catalyse the synthesis of both straight and coiled or twisted CNFs. Like La and Ni, Au also supported a tip-growth mechanism as Au particles were also observed on many of the tips of the CNFs as the Au particles were dislodged from the RANR support. Temperature facilitated enhanced sintering and the dislodged Au nanoparticles grew to larger particles of different sizes. The sintered nanoparticles determined the diameters of the CNFs synthesized. The fibres synthesized under different parametric conditions ranged from 10–100 nm in thickness with an average diameter of 50 nm. Detailed studies also showed that both the diameter and length distribution range increased drastically with increase in reaction temperature. The temperature enhanced decomposition of C_2H_2 and thus more carbon was available for forming the carbon matrix of the CNFs.

La and Ni were co-loaded on RANR to form a co-loaded La-Ni/RANR catalyst. Metal wt. % loadings ranging from 1-10 wt. % were achieved. The peaks identifying La may be ascribed to $La(OH)_3$ and La_2O_3 phases while Ni peaks were due to NiO. The phases reduced to metallic La and Ni to give co-loaded La-Ni/RANR catalysts. Reduction peaks shifted to higher temperatures with an increase in metal nanoparticles wt. % loading. The shift in the peak positions to higher temperatures may be attributed to increased crystallinity of the metal oxides and mainly the increase in the oxygen in the metallic matrix of the catalysts. The Ni nanoparticles were characterised by a spherical morphology with a diameter range of 1–6 nm

with an average of 4 nm. The short rod structured nanoparticles were those of La with a diameter range of 2–8 nm and an average of 7 nm. The co-loaded La-Ni/RANR catalysts catalysed the synthesis of CNFs that were a mixture of both straight long stretching nanofibers and twisted or coiled nanofibers. The actual morphology of each individual CNF may have been directly attributed to the surface or end of the La-Ni nanoparticle over which it grew. The straight chain CNFs were catalysed by the La end of the co-loaded La-Ni/RANR catalyst, while the coiled or twisted CNFs, were catalysed by the Ni end of this catalyst. During CVD reaction, the respective metal nanoparticles also dislodged from the support, sintered and gave synthesised fibres with a diameter range of 50–500 nm with an average of 175 nm. It was observed that there were no synergistic effects as a result of co-loading La and Ni on the RANR support.

The supported catalysts, La/RANR, Ni/RANR, Au/RANR, and La-Ni/RANR showed exceptional performance as catalysts in the synthesis of CNFs. However, the plain RANR had no catalytic effect observed during the CVD synthesis of SCNMs. TiO₂ is well known for its excellent photocatalytic behaviour. Therefore the supported catalysts and the plain RANR were compared as catalysts for photocatalytic degradation of methyl orange (MeO). Detailed studies of the preparation of the supported catalysts revealed that metal loading did not result in the blending of the nanoparticles species into the rutile phase lattice of the RANR. Both PXRD and LRS showed the RANR peaks dominating those of the supported nanoparticles. The supported metal nanoparticles caused slight shifting of the RANR peak positions. The low wt. % supported catalysts did not show any significant photocatalytic activity different from that of pure RANR. A 5–8 wt. % loading was observed to be ideal for the photodegradation of MeO. La/RANR showed the highest photocatalytic performance of all the supported catalysts. However, plain RANR exhibited excellent photocatalytic activity, with degradation efficiency that far exceeded that of the whole range of supported catalysts. The co-loaded La-Ni/RANR was the worst photocatalysts due to a combination of Ni inactivity and a tendency to inhibit the photocatalytic activity of both La and plain RANR. Photoluminescence studies exhibited reduced intensities for the supported catalysts indicating consequential effective prohibition of recombination of the electrons and respective holes. However, La/RANR sufficiently slowed the radiative recombination process of photogenerated electrons and holes in TiO₂. This is because La loaded TiO₂ has a tendency of expanding the wavelength response range as determined by diffuse reflectance UV-Vis spectroscopy.

Figure 1.1 (a)-(d). Typical FESEM images of the products synthesised with a titanium *n*-butoxide TNB concentration of 0.4 M at various reaction temperatures: (a, b) 120 °C, (c, d) 150 °C, (a) and (c) are overview FESEM images (b) and (d) are enlarged FESEM images of the surfaces of the corresponding samples.⁷ 10

List of Abbreviations

(+) AuNPs – Positively-charged gold nanoparticles

AD – Arc-discharge

AuNPs – Gold nanoparticles

BET – Brunauer–Emmett–Teller

BSE – Back scattered electrons

CA – Citric acid

CCD – Charge-coupled device

CCVD – Catalytic chemical vapour deposition

CdS – Cadmium sulphide

CECVD – Catalyst-enhanced chemical vapour deposition

CL – Cathodoluminescence light

CNFs – Carbon nanofibers

CNHs – Carbon nanohorns

CNSs – Carbon nanospheres

CVD – Chemical vapour deposition

DP – Deposition-precipitation

DPU – Deposition-precipitation using urea

DRS – Diffuse reflectance spectroscopy

EDS – Energy dispersive X-ray spectroscopy

EPMA – Electron probe microanalysis
FCCVD – Floating catalyst chemical vapour deposition
FESEM – Field emission scanning electron microscopy
FIB – Focus ion beam
FTIR – Fourier transform infra-red
HRTEM – High resolution transmission electron microscopy
ICSD – Inorganic crystal structure database
IP – Isoelectric point
LA – Laser ablation
LLIF – large lithium fluoride
LPET – large pentaerythritol
LRS – Laser Raman spectroscopy
MeO – Methyl orange
MWCNTs – Multi-walled carbon nanotubes
NiPd – Nickel palladium
PECVD – Plasma-enhanced chemical vapour deposition
PL – Photoluminescence
PC0 – pseudocrystal zero
PZC – Point of zero charge
RANR – Radially aligned nanorutile
SCNMs – Shaped carbon nanomaterials
SE – Secondary electrons
SEM – Scanning electron microscopy
SiNWs – Silicon nanowires
SNMs – Shaped nanomaterials
SWCNTs – Single-walled carbon nanotubes
TEM – Transmission electron microscopy
TGA – Thermogravimetric analysis
TNB – Titanium *n*-butoxide

TPO – Temperature programmed oxidation

TPR – Temperature programmed reduction

UV/Vis – Ultraviolet and visible spectroscopy

VTPXRD – Variable temperature powder X-ray diffraction

WDS – Wavelength dispersive spectroscopy

WGSR – Water gas shift reaction.

Conference presentation

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The work presented in this thesis has been presented at international and national conferences.

- ❖ Dziike, F., Franklyn, P.J. and S.H. Durbach. *Synthesis of shaped carbon nanomaterials from supported Au, Ni and La catalysts on nanodandelions. **Poster presentation.*** Department of Science and Technology/Centre of Excellence in Strong Materials (DST/CoE-SM), Student Presentation Workshop 2014. University of the Witwatersrand, South Africa, May 2014.
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- ❖ Dziike, F., Franklyn, P.J. and S.H. Durbach. *Synthesis of SCNMs on Au, La and Ni catalyst nanoparticles supported on rutile dandelions. **Poster presentation.***

Cross Faculty Student Presentation 2015. University of the Witwatersrand, South Africa, October 2015.

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- ❖ Dziike, F., Franklyn, P.J. and S.H. Durbach. *Preparation of CNMs on Au, La and Ni dandelions. Oral presentation.* The 52nd Annual Conference of the Microscopy Society of Southern Africa (MSSA) 2015. Pretoria, South Africa, 29 November-5 December 2015.
- ❖ Dziike, F., Franklyn, P.J. and S.H. Durbach. *Tailored synthesis of SCNMs on Au, La and Ni catalyst nanoparticles supported on novel rutile dandelions. Poster presentation.* Department of Science and Technology/Centre of Excellence in Strong Materials (DST/CoE-SM), Student Presentation Workshop 2016. University of the Witwatersrand, South Africa, May 2016.

Chapter 1

1.1 Introduction

Carbon materials have been synthesised at the nano-size in many different shapes including: spheres, coils, tubes, fibers and helices.¹ Among these shaped carbon nanomaterials (SCNMs) are the group known as carbon nanotubes (CNTs). CNTs are composed of graphene sheets rolled into seamless cylinders (i.e. a single-walled carbon nanotube (SWCNT) for a single sheet or multiple cylinders nested within each other i.e. multi-walled carbon nanotubes (MWCNTs)).²⁻⁴ Carbon nanofibers (CNFs) are cylindrical nanostructures with graphene layers packed as stacked sheets while CNTs are cylindrical rolled up sheets of carbon atoms. Interest in the synthesis of SCNMs has increased as more discoveries and a wide range of advanced uses of these nanomaterials has occurred. SCNMs such as SWCNTs, carbon nanohorns (CNHs), carbon nanospheres (CNSs), MWCNTs and carbon nanorods, exhibit outstanding mechanical, electronic, optical, and thermal properties.¹ They are also characterised by large active surface areas, good conductivities, chemical stabilities and have been used as a host material for the loading of noble metal materials for various applications.⁵

The synthesis of SCNMs has been carried out using many different methods and reaction conditions. For example, chemical vapour deposition (CVD) has been commonly used as an alternative to laser ablation (LA) and arc-discharge (AD). Recent research has attempted to investigate catalysts that provided efficient ways of synthesising SCNMs at low costs.⁶ Here metal oxides were used as supports of the desired catalyst for the synthesis of SCNMs.⁶ These catalysts were deposited using deposition-precipitation (DP) techniques or were prepared using other chemical methods such as deposition-precipitation using urea (DPU).⁶

Titania (TiO_2) is a metal oxide that has been frequently used in its nanostructured form as a catalyst support.⁷ Studies have revealed that the morphology and crystal form of such nanostructured materials had to be controlled, as their properties and performance were greatly dependent on these.⁸⁻¹² For instance, when TiO_2 was assembled into three-

dimensional nanostructures, it was shown to have unique properties and characteristics, including: novel topology, ion-exchangeable ability as well as photocatalytic ability.¹³ Hence the idea for this thesis is that under the correct conditions, specific nanostructures of TiO₂ may be successfully used as supports for metals (Au, Ni, La,) active for the synthesis of SCNMs.

Recent research has shown that TiO₂ could be synthesised in the form of dandelion-like nanostructures that were made up of rutile nanorods that were radially aligned and had diameters of 1 μm (**Fig. 1.1 ((a)-(d))**).⁷ These structures were prepared from a mixture of 0.4 M titanium *n*-butoxide (TNB) and 0.9 M HCl when added to *n*-hexane in a total volume of 26 ml and reacted solvothermally under stirring at 120 – 210 $^{\circ}\text{C}$ for 4 h.⁷

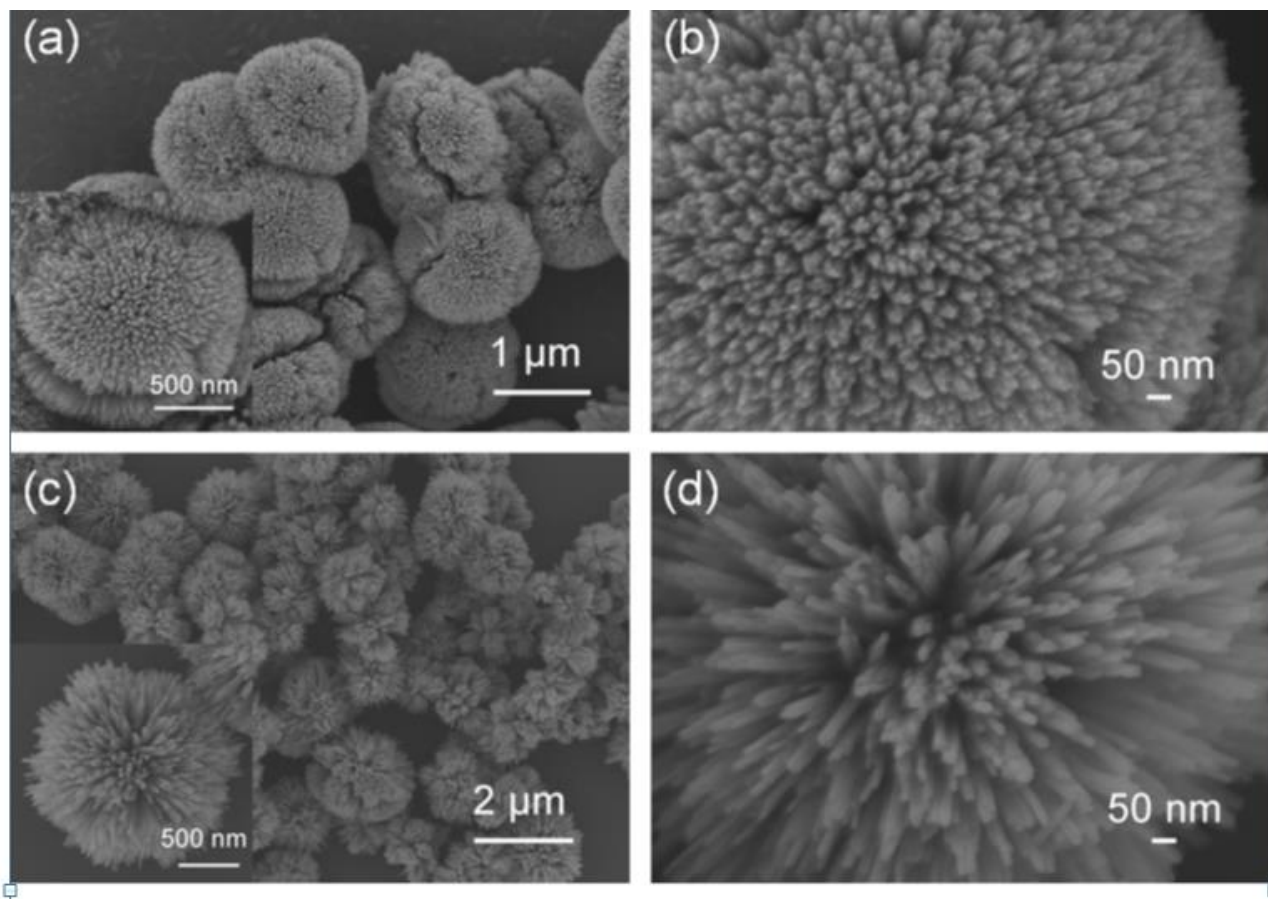


Figure 1.1 (a)-(d). Typical FESEM images of the products synthesised with a titanium *n*-butoxide TNB concentration of 0.4 M at various reaction temperatures: (a, b) 120 $^{\circ}\text{C}$, (c, d) 150 $^{\circ}\text{C}$, (a) and (c) are overview FESEM images (b) and (d) are enlarged FESEM images of the surfaces of the corresponding samples.⁷

In a similar vein, research conducted in our laboratories has shown that radially aligned nanorutile structures (RANR) (see Fig.4.2), could be reproducibly synthesised by an alternative hydrothermal technique (see Section 4.2.1). In this work, RANR were prepared in such a way that the rutile nanorods that formed had an average diameter of 5–8 nm and lengths which ranged from 300–650 nm. These rutile nanorods were assembled together in the form of microspheres and in subsequent studies in this thesis their square-shaped tips were used as support surfaces in the DP of: gold, nickel and lanthanum and lanthanum–nickel mixed metal nanoparticles. Thereafter these metal/RANR assemblies were tested as catalysts for the CVD synthesis of SCNMs. Investigations in this work sought to determine what wt. % loading of each of these metals was required to effect optimal conditions for the synthesis of SCNMs. Furthermore these studies were focused on deposition of the smallest possible particles to increase their reactivity and on the development of a workable method for the selective synthesis of SCNMs.

1.2 Aim and Objectives

1.2.1 Aim

The main aim of this thesis was to establish if SCNMs could be synthesised by CVD over gold (Au), nickel (Ni), lanthanum (La) and lanthanum-nickel (La-Ni) when deposited on novel RANR supports. Here the catalyst preparation technique i.e. the hydrothermal synthesis of the RANR support and then the subsequent DP of these metal nanoparticles was subject to detailed study. Through the research in this thesis it was also sought to determine the nature of the carbon nanomaterials that could be synthesised over these catalysts with specific respect to: CNHs, CNTs, CNFs, CNSs, SWCNTs and MWCNTs. Further application was extended by testing the supported catalysts and the plain RANR in photocatalytic degradation of an organic specimen.

1.2.2 Objectives

The objectives of this thesis were to:

- Prepare RANR by a facile hydrothermal synthesis method.
- Load Au, Ni and La nanoparticles onto the RANR support by DPU.
- Determine the crystallographic properties of the metal/RANR catalysts.
- Ascertain the optimum stable wt. % loading of the supported metals that would have the highest catalytic performance in the CVD synthesis of SCNMs.
- Determine the optimal conditions for the synthesis of the SCNMs using CVD.
- Characterise both the catalysts prepared and the SCNMs synthesised under the optimal conditions.
- Test photocatalytic performance of the supported catalysts against plain RANR supported material.

1.3 Research Justification

The pre-eminent technical issue in the preparation of supported catalysts is to optimise DP conditions to target catalytic properties that greatly affect their characteristics and performance. DP techniques directly influence the nanoparticles' characteristics such as: particle size, morphology, purity, and the chemical composition of the catalyst deposited on the support.¹⁴ The key element to DP is the use of low pH and temperature to bring about slow deposition-precipitation of the precursor metal hydroxides onto the support while allowing a high wt. % of metal to be deposited. Hence a detailed study of the optimal DP conditions of these selected metal nanoparticles (i.e. Au, Ni and La) could bring about the desired CVD synthesis of SCNMs. The choice of the metals was carefully done considering their positions on the periodic table. Ni is known to catalyse the synthesis of CNMs. Its behaviour was tested on the unique RANR support and compared to a higher transition metal, Au. Further testing was taken to a different metal group, La and effect of co-loading tested on La-Ni lanthanide-transition system. However the TiO₂ used to make the RANR support is known for its photocatalytic activity. Effect of loading Au, Ni, La and La-Ni on RANR may further be studied by comparing the photocatalytic behaviour of the supported catalysts to that of plain RANR.

1.4 Scope of the Research

Research was conducted in this thesis to investigate the preparation as well as characterisation of RANR, using a facile hydrothermal synthesis method, as a support for metal nanoparticles in the CVD synthesis of SCNMs. The dependence of RANR attributes on the preparation conditions and on the post-treatments significantly dominated the feasibility of its application as a support to precursor metal catalysts of interest. Hence work reported in this study concentrated on:

- The synthesis and subsequent characterisation of RANR by a hydrothermal synthesis method (Chapter 4)
- The synthesis and characterisation of Au, Ni and La loaded on RANR by DP (Chapter 4)
- The use of Au, Ni and La loaded RANR for CVD synthesis of SCNMs (Chapters 5-8)

- The evaluation of the photocatalytic properties of Au, Ni and La loaded on RANR (Chapter 9)

The chapter which follows provides a theoretical framework to the work that was performed in the above-mentioned chapters, as well as a thorough review of the related literature.

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Chapter 2

2.1 Literature review

2.1.1 Titanium dioxide (TiO_2)

TiO_2 occurs in several polymorphic forms. The two most common are anatase and the more thermodynamically stable rutile phase (as seen in **Fig. 2.1**).

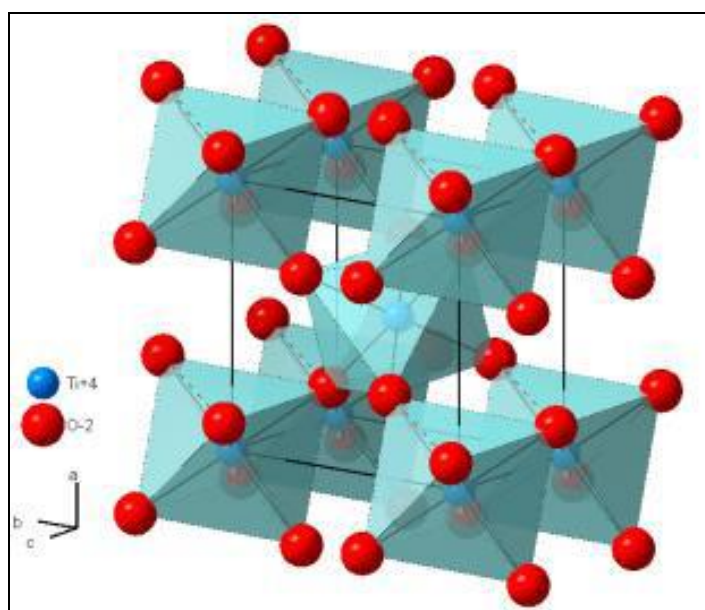


Figure 2.1 Rutile unit cell, showing central Ti(IV) ion with 6 coordinating oxygen ions at the apexes of an octahedron.¹

Pure TiO_2 in the crystalline rutile phase is characterised by semiconducting properties and has a photocatalytic activity of great importance in energy storage and environmental pollution control.² TiO_2 , as a semiconductor photocatalyst, has received a great deal of attention due to its chemical stability, non-toxicity, low cost, and other advantageous properties. However, a major disadvantage to its wide-scale use is its ineffectiveness under visible-light irradiation i.e. the band gap of anatase is 3.2 eV, which requires excitation wavelengths of < 387.5 nm. This implies that there remains a challenge with respect to extending the photocatalytic response of TiO_2 in the visible region.³ In addition, the photocatalytic activity of TiO_2 is limited by fast charge carrier recombination and low interfacial charge-transfer rates of photo-generated carriers.²

However, TiO_2 exhibits a wide range of potential technological applications, including: photocatalysis of pollutants, photo-splitting of water and transparent conducting electrodes for dye-sensitized solar cells.⁴ Titania is used in different morphological forms. These include nanoparticles, nanorods, nanowires, nanospheres and nanotubes. For instance, 3D titania hierarchical structures with hollow spheres and agglomerated spheres have also been recently synthesized.⁵ Similarly titania nanoflowers have been synthesized by oxidising pure Ti with hydrogen peroxide solutions at low temperature.⁶ On the other hand, Fujihara and Jiang have separately synthesized 3D titania hierarchical structure films on glass substrates with nanorods that were radially arranged.^{7–10}

Research has shown that facile hydrothermal methods of synthesis, can oxidatively convert Ti(III) to Ti(IV) and hence make 3D dandelion-like nanostructures with TiCl_3 as the precursor material. For example, when titanium(III) chloride was dissolved in HCl to make an aqueous solution containing 15 wt% of TiCl_3 and supersaturated using NaCl or NaOH to control the pH of the solution, then 3D dandelion-like nanostructures were formed after the solution was heated at $200\text{ }^\circ\text{C}$ for 4 h.¹¹ A schematic diagram illustrating the growth mechanism of the 3D dandelion-like nanostructures under various experimental conditions of the hydrothermal method of synthesis is shown in **Fig. 2.2**.¹¹

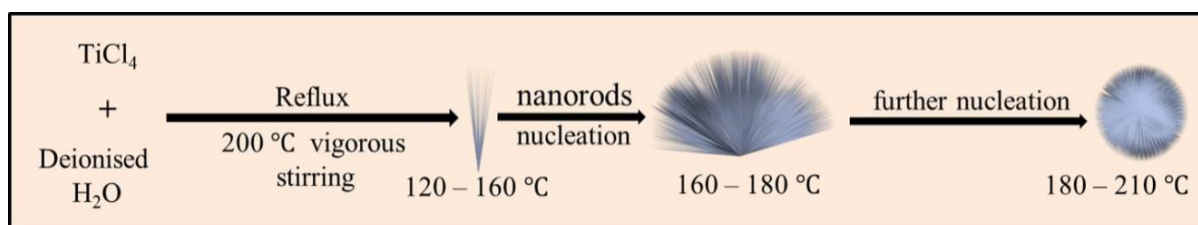


Figure 2.2. Schematic illustrations of the growth mechanism of the 3D dandelion-like nanostructures under various experimental conditions.¹¹

The FESEM images of the centrifuged, washed (with water and pure ethanol) and room temperature dried dandelion-like spheres that were produced by the hydrothermal method are shown in Fig 2.3.¹¹

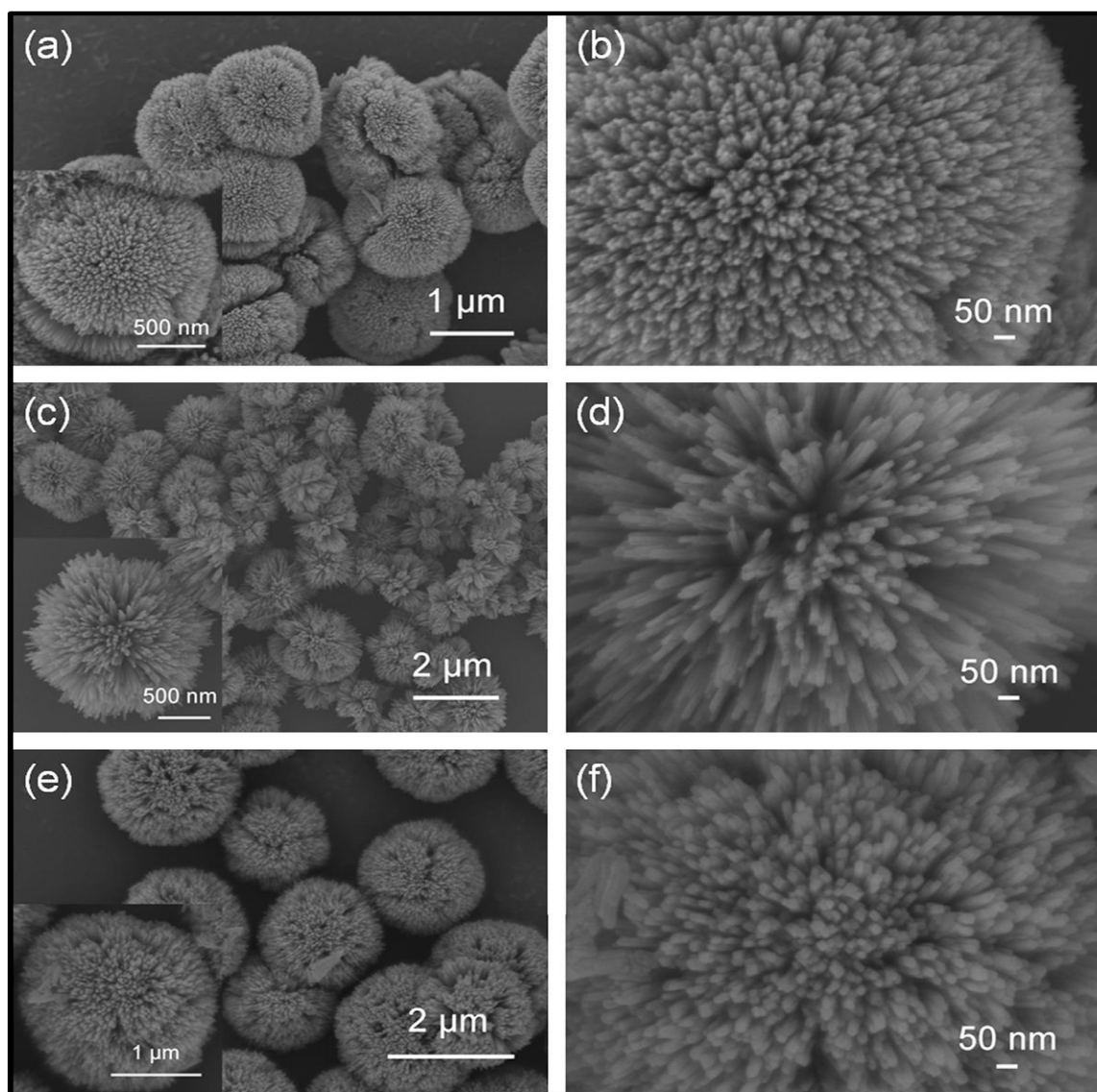


Figure 2.3 Typical FESEM images of the products synthesized with 0.4 M TNB at reaction temperatures ranging from 120 – 210 °C.¹¹

Rod-like structures formed around a central particle, similar to the RANR microspheres shown in this thesis, have been synthesized from metallic materials such as silicon nanostructures (SiNWs), calcium carbonate and iron(III) oxide prepared by sol-immobilization, solvothermal and hydrothermal methods respectively.^{12–14} However a thorough search of the literature has revealed that none of these have been used or tested as catalyst supports in the synthesis of SCNMs.

In this study, the RANR structures which were synthesized by a hydrothermal synthesis method (see **Section 3.1.1**) were used as supports onto which metals were preferentially deposition-precipitated. Thereafter the metal/RANR assemblies were used as catalysts for the

synthesis of SCNMs. The metals that were loaded onto the RANR supports by DP will be discussed in **Sections 2.1.2 – 2.1.5** which follow.

2.1.2 Lanthanum (La) as a catalyst

Research has shown that TiO_2 doped with La^{3+} , prepared by the sol–gel method, was more stable and had higher crystallinity than TiO_2 prepared by the hydrothermal method.¹⁵ In the former case it was found that the La^{3+} doped ions more easily entered the lattice of TiO_2 , where it was postulated that they replaced some of the Ti^{4+} ions to form Ti-O-La at the interface.¹⁶ Consequently La is believed to form a very stable supported catalyst on TiO_2 i.e. La/TiO_2 . Previous research has also found that La doped TiO_2 presented high visible-light performance, while co-dopants like: carbon, nitrogen and boron enhanced the photocatalytic activity.^{15,17–20} In at least one case it was believed that doping TiO_2 with La^{3+} accelerated the separation of photo-generated electrons and holes, while the co-dopant narrowed the band gap and improved the quantum light efficiency.²¹ **Section 5.2** presents further detailed applications of La based catalysts.

2.1.3 Nickel (Ni) as a catalyst

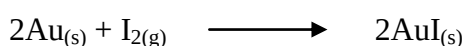
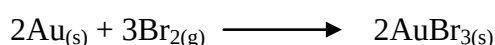
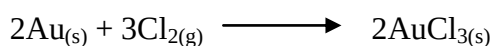
The good performance of Ni-containing catalysts has been suggested to be due to: increased dispersion of the active phase, increased acidity, improved sulfurability or reducibility, induction of edge-on XS_2 crystallites and state of the promoter.¹⁸ As an example, a sol-gel method has been used to obtain a precursor gel to prepare Ni_x/TiO_2 from titanium isopropoxide and nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$).¹⁸ In order to obtain the Ni_x/TiO_2 films, the precursors were dissolved in 2-propanol under vigorous stirring to get a sol. Thereafter 1 ml of nitric acid was added dropwise until the sol began forming a gel.¹⁸ The resultant gel was spun onto glass substrates to deposit these thin films which were then annealed.¹⁸ A detailed review of the applications of Ni in different catalytic forms and reactions has been presented in **Section 6.2**.

2.1.4 Gold (Au) as a catalyst

Gold's electronic structure is $[\text{Xe}] 4f^{14}5d^{10}6s^1$. This configuration ensures that the 4f electrons under-screen the 5d, 6s and 5p electrons from the nuclear charge resulting in a lanthanide contraction¹³. This contraction in turn results in the 5d metal series having similar lattice constants to that of the 4d metals. In heavier elements such as gold, there is also a relativistic factor that must be taken into account as the velocity of the 1s electrons begin to approach the

speed of light¹³ The mass of the electrons therefore increases relativistically, resulting in a contraction of their orbitals around the nucleus. Due to this, the higher s and p orbitals also contract, including the higher 6s and 6p orbitals that results in these orbitals being smaller than they usually would have been.¹⁵ The final result of all these effects are that the 5d and 5f orbitals expand outwards and are thus destabilised, which in turn, has an associated increase in energy as a consequence of relativistic modification of the valence responses explainable by double perturbation theory.¹⁵

Gold is a soft metal that is largely unreactive and highly stable even on lengthy exposure to air, water, and other chemicals in the environment. The most common oxidation states of Au are Au(I) and Au(III) and to lesser extent Au(V). The Au(III) has the d^8 configuration which gives rise to many square planar complexes. The Au(I) has the d^{10} configuration and is prone to the formation of linear structures. This phenomenon is manipulated in its extraction, where it is reacted with HCN to give a cyanide complex $[Au(CN)_2]$. Gold is characterised by a high electronegativity with a value of 2.4 and a quite significant electron affinity of about 223 kJ mol^{-1} giving Au^+ ionic salts. Gold reacts with halides to form trihalides with Cl and Br, while forming a monohalide with iodine.¹⁶



Gold readily reacts with acids but does not react with aqueous bases. In its crystalline state, gold has a cubic close-packed structure with a closest Au-Au separation of 288.4 pm, implying a gold metallic radius of 144.2 pm.²⁰ Because of its stability under normal conditions, Au (in its bulk form) has for a long time been considered to be catalytically inactive for a long period of time. However, most recently supported gold nanoparticles (AuNPs) have been used as highly active catalysts for a number of selective oxidation reactions, such as: water gas shift (WGSR) reactions, epoxidation of propene, oxidation of alcohols to aldehydes and oxidation of D-glucose.¹⁷

AuNPs supported on TiO_2 have been tested as photocatalysts for the production of hydrogen.¹⁸ The step-wise scheme outlined below has been proposed to explain the high

photocatalytic activity of this TiO_2 catalyst which produced hydrogen through methanol/water decomposition:¹⁸

- (1) $\text{TiO}_2 + 2h\nu \longrightarrow \text{TiO}_2(2e^- + 2h^+)$
- (2) $2h^+ + \text{H}_2\text{O}_{(\text{liq})} \longrightarrow \frac{1}{2}\text{O}_{2(\text{g})} + 2\text{H}^+$
- (3) $2\text{H}^+ + 2e^- \longrightarrow \text{H}_{2(\text{g})}$
- (4) $2h^+ + \text{CH}_3\text{OH}_{(\text{liq})} \longrightarrow 2\text{H}^+ + \text{HCHO}$
- (5) $\text{CH}_3\text{OH}_{(\text{liq})} \longleftrightarrow \text{HCHO}_{(\text{g})} + \text{H}_{2(\text{g})}$
- (6) $\text{HCHO}_{(\text{g})} + \text{H}_2\text{O}_{(\text{liq})} \longleftrightarrow \text{HCO}_2\text{H}_{(\text{liq})} + \text{H}_{2(\text{g})}$
- (7) $\text{HCO}_2\text{H}_{(\text{liq})} \longleftrightarrow \text{CO}_{2(\text{g})} + \text{H}_{2(\text{g})}$
- (8) $\text{CH}_3\text{OH}_{(\text{liq})} + \text{H}_2\text{O}_{(\text{liq})} \longleftrightarrow \text{CO}_{2(\text{g})} + 3\text{H}_{2(\text{g})}$

It is thought that the effectiveness of this type of photocatalyst might in part be due to the deposition of the gold by DPU, as this method allows for the formation of homogeneous AuNPs in close interaction with TiO_2 .

A diagram showing the proposed effect of the presence of AuNPs on a TiO_2 surface is shown in **Fig. 2.4**.⁹ Here the mechanism proposed starts with the excitation of TiO_2 by UV–Vis light to form an electron (e^-) – hole (h^+) pair (1) shown in the series of steps above.⁹

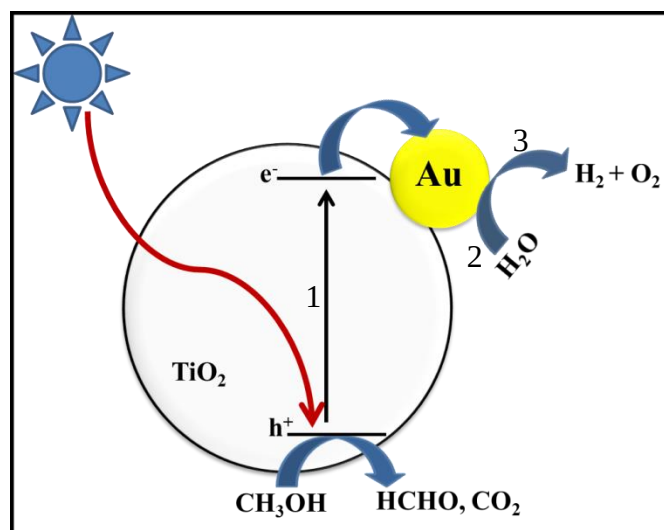


Figure 2.4. A proposed mechanism for H_2 production by Au/TiO_2 photocatalysts through methanol/water decomposition.⁹

The splitting of water molecules is then induced to release oxygen and hydrogen ions (2).⁹ The electrons generated on the TiO_2 surface are then transferred to AuNPs where hydrogen

ions are reduced to hydrogen gas (3).⁹ The effect of the AuNPs on titania is suggested to be for attracting the electron charge to their surfaces, avoiding the bulk or surface recombination of the $e^- - h^+$ species, thereby promoting the formation of atomic species of oxygen and hydrogen.⁹ In the above-mentioned study, the optimal loading of gold onto the TiO_2 surface was found to be 0.5 wt. %.⁹ Here it was found that thermally treating Au/TiO_2 at 300 °C produced AuNPs with the best homogeneity and catalysts with the highest photocatalytic activity.⁹ Significantly, the photocatalytic activity was highest in the Au/TiO_2 catalysts when gold was in its metallic state.⁹ Conversely, oxidised gold seemed to have had a detrimental effect on the photocatalytic activity of the material.¹⁹

Gold is known to undergo oxidative transformations under different temperature conditions and chemical environments.¹⁶ **Fig. 2.5** shows the variation of the particle size of the AuNPs upon different treatment conditions.

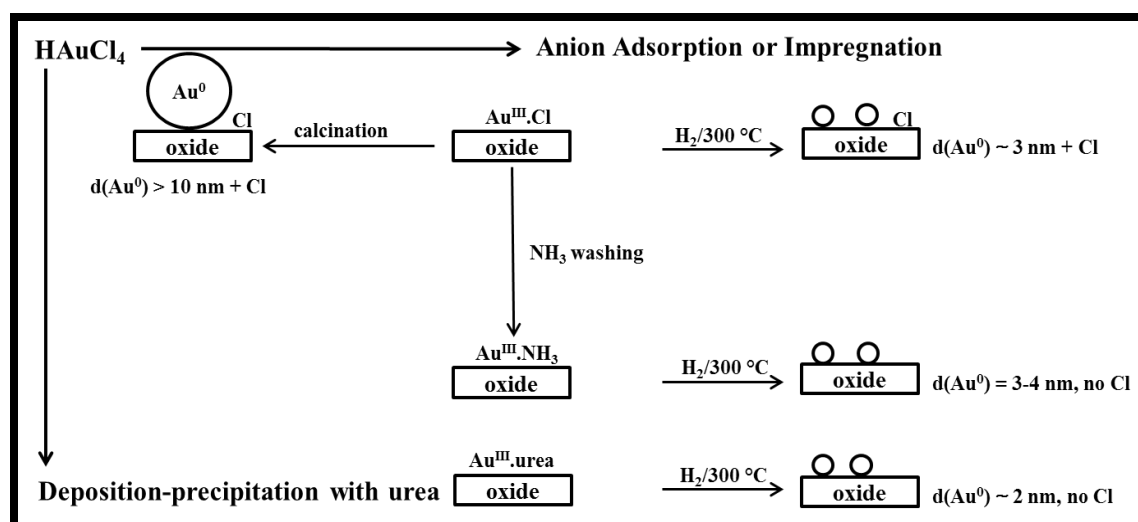


Figure 2.5 Mechanism for the preparation of supported gold catalysts by anion adsorption or impregnation and DPU.²⁰

The use of AuNP-based catalysts has been widely explored in recent years.¹¹ Detailed analysis and studies have demonstrated how the catalytic performance of supported gold catalysts was dependent on the particle sizes of the AuNPs.¹¹ Hence, their role in the reaction mechanism and their active sites when used as catalysts was found to be subject to their: dispersion, interaction with the support and the characteristics of the support.²¹ AuNPs deposited on inert materials have shown catalytic activity for the synthesis of CNTs only when their diameters were between 2–10 nm.²¹ On the other hand, when AuNPs with diameters from 2 to 26 nm were supported on transition metal oxides (such as ceria-

zirconium oxide, iron oxide, etc.) they exhibited excellent catalytic performance for applications in: chemical processing, pollution control and fuel cells.¹⁴ Additionally, AuNP-based catalysts (such as Au/Fe-oxide, Pt-Au/Fe₂O₃, Au supported on Co₃O₄, NiO, ZnO, ZrO₂, CeO₂ and Ti-SiO₂) have enabled low reaction temperatures (20 – 100 °C) to be used and have provided high reaction selectivity for CO oxidation.²² The preparation of AuNP-based catalysts has been shown to be affected by at least two factors. The first was the amount of Au that could be deposited, which was significantly affected by the point of zero charge (PZC) of the oxide support.²³ The second was the source of the Au. Here, since a number of Au sources were chloroauric compounds, it has been found that the trace amounts of residual Cl⁻ were able to negatively influence the catalytic activity of these AuNP-based catalysts.²⁴

2.1.5 Lanthanum-Nickel (La-Ni) co-loaded on RANR

Recent research, involving new combinations of elements for use as catalysts, has sought to develop stable, highly efficient and active catalytic materials.²⁷ For instance, transition metals of group VIIIB like: Ni, Co, Pd, Ir and perovskite type oxides such as LaNiO₃ have been reported to be very active catalysts.³¹ Ni-containing catalysts are said to bring about excellent performance with high long-term stability, have sintering resistance and are able to evade deactivation.^{32–34} Nickel containing mixed-metal catalysts have also been prepared on different support materials such as: TiO₂, SiO₂, γ -Al₂O₃, ZrO₂ and La₂O₃ and have demonstrated high efficiency as well as reliability, even at high temperatures (973 – 1173 K) for reactions such as the steam reforming of methane.³¹ Similarly Ni with La in the La-Ni/Al₂O₃ mixed-metal catalyst have been shown to stabilize alumina high temperature applications.³⁵ Lanthanum has also been found to bring about a synergistic effect in catalysts by improving their resistance to coking in the steam reforming of: propane and ethanol as well as in dry reforming.^{27,36,37} Similarly, in methane reforming reactions a perovskite type LaNiO₃ mixed-metal catalyst has been used as a precursor for a very active catalyst in the CO₂ reforming of CH₄.^{38,39}

Detailed studies have also investigated the stabilities and activities of perovskite La₂NiO₄, where their performance was compared against the polymorphic phases of LaNiO₃ and Ni/La₂O₃.⁴⁰ In a related study a simple self-combustion method was used to prepare perovskites from their respective precursor compounds.⁴¹ Here highly dispersed metal nanoparticles were formed in situ over a titania support which resulted in high catalytic activity and stability.⁴¹

Since a highly stable support material, especially with refractory properties, sustains its catalytic behaviour under both reducing conditions and high temperature reactions, it was decided to test this phenomenon using a novel support material i.e. radially aligned nanorutile (RANR), in the form of microspheres. The RANR provided a unique topology onto which LaNi mixed-metal catalysts were homogeneously dispersed. However, unlike in the above-mentioned study, the catalyst was not formed in situ during the CVD reaction, but rather during the catalyst preparation step in deposition-precipitation where urea was used. Some of the deposition-precipitation methods will now be discussed.

2.2 Deposition-precipitation (DP) methods.

Gold precursors have been deposited on TiO_2 by: cation adsorption (CA), deposition-precipitation with urea (DPU) and NaOH (DPOH) to form Au/TiO_2 catalysts. Detailed studies have been carried out to determine the nature of the species deposited as well as the chemical phenomena which occurred during their preparation. It has been shown that the cationic adsorption of the $[\text{Au}(\text{en})_2]^{3+}$ complex had to be carried out at room temperature to avoid the decomposition of the complex and the reduction of gold.⁴² DPOH and DPU methods have involved the deposition of a Au(III) species on a TiO_2 surface.¹⁹

Deposition-precipitation with NaOH (DPOH) developed by Haruta¹⁴ presented better results in terms of catalytic activity than impregnation which led to large AuNPs (>10 nm).^{43,44} DP with NaOH is easier to carry out than with urea and is efficient in preparing nanosized gold particles (2-3 nm) with deposition approximating 8 wt.% at a pH close to the point of zero charge of the oxide ($\text{PZC}_{\text{TiO}_2} \sim 6$).⁴⁵ Further attempts to increase gold loading can be achieved by decreasing the pH of the solution below 6 but this will be at the expense of the gold particle size which increases sharply and also less gold particles loading onto the support.^{45,46}

Gold catalysts are effective at low reaction temperatures. This phenomenon was tested and observed for the oxidation of CO and the decomposition of trimethylamine.³⁸ The particle size of gold on the metal-oxide supports could be controlled by the selection of a suitable calcination temperature. Smaller-sized AuNPs (<5 nm) gave the highest catalytic activity and this posed an added advantage of the use of lower calcination temperature.⁴⁷ It was observed that the formation of large particles results from the fact that the interaction of HAuCl_4 with the support is weak. The chlorides in the samples promote sintering of the Au particles during thermal treatment. The sintering is suggested to be due to the high mobility of Au on the support in the presence of chlorides.⁴⁵

The particle size and the amount of gold deposited on TiO₂ strongly depend on the pH of the solution containing the HAuCl₄. In most preparation methods, Au is in the oxidation state 3+ after drying. The thermal treatment used to reduce Au^{III} into Au⁰ can be performed with any reducing gas such as H₂ or oxidising gases such as air. When the supported gold precursor decomposes in air with temperature, it forms Au⁰ because of the instability of Au₂O₃.⁴⁸

Haruta *et al* developed a deposition-precipitation method using sodium hydroxide (DPOH).¹¹ The method proved more viable than the conventional deposition of organogold complex in gas or liquid phase on a support in the absence of moisture. It is also an efficient method to prepare nanosized gold particles (2-3 nm). However, the method is not effective for the deposition of gold nanoparticles on metal oxides with a point of zero charge (PZC) below 5 or on activated carbon.⁴⁹ The totality of gold present in solution cannot be deposited on the support using DP with NaOH. Maximum gold loading as low as ≤ 3 wt. % has been reported to be deposited by DP with NaOH at pH range 7 – 10, when the nominal amount of gold present in solution of 13 wt. %.⁴¹ However, gold loading is reportedly higher ≈ 8 wt. % at a pH close to PZC_{TiO₂} which occurs at ~ 6 in DP with urea. Previous studies reported that deposition-precipitation with urea, coupled with increased DP time in solution led to small Au particle sizes (2-3 nm) even at a very high metal loading.^{50,51}

The DPU preparation is characterised by the deposition of gold onto the TiO₂ surface from the precipitation of a gold compound. The gold deposition on the TiO₂ proceeds by way of formation of gold-titania surface complex, and then of gold colloids arising from the reduction of Au^{III} species by the Ti³⁺ ions present in the support.⁴³ The gold colloids are negatively charged on the surface and interact with the positively TiO₂ surface at low temperature.^{45,47} R Zanella *et al.* carried out detailed studies on different ways of carrying out deposition precipitation of gold catalyst nanoparticles.^{17,19,48,52–54}

2.3 Synthesis of carbon nanomaterials

Carbon nanomaterials have been synthesized using various techniques including: chemical vapour deposition (CVD), laser ablation (LA), and arc-discharge.⁴⁹ The need for the synthesis of shaped carbon nanotubes or nanomaterials is primarily because of their outstanding mechanical, electronic, optical and thermal properties.^{55,56} CVD shows noticeable advantages for the growth of shaped carbon nanotubes or nanomaterials in terms of low growth temperature, good controllability, and easiness to scale up product yield and increase purity. Laser ablation and arc-discharge could grow shaped carbon nanotubes or nanomaterials at a

relative high yield.⁵⁶ An improved floating catalyst CVD (FCCVD) was developed for the semi continuous synthesis of shaped carbon nanotubes or nanomaterials with a relatively large scale, high purity and low cost.⁵⁵

FCCVD involves aligning two horizontal tube furnaces with two temperature zones in the reaction tube for the growth of shaped carbon nanotubes or nanomaterials. Benzene can be used as a carbon source and H₂ is used to bubble the benzene into the reaction tube. The catalyst precursor is ferrocene which vaporises and decomposes at low temperature to form atomic Fe which then agglomerates into iron-clusters or nanoparticles.⁵⁷ A growth promoter, (thiophene) is added in a small amount by dissolving it in the benzene and then serve to nucleate shaped carbon nanotubes or nanomaterials.⁵⁸ Ferrocene is consumed in the growth process and the synthesized shaped carbon nanotubes or nanomaterials are floated and transferred by the carrier gas to hang onto the reaction tube wall. The shaped carbon nanotubes or nanomaterials are then continuously grown through the floating catalyst method. The method produces a large quantity of web-like, silver black, very light and free standing shaped carbon nanotubes or nanomaterials.⁵⁷ The structures of the carbon nanomaterials can easily be tuned and systematically adjusted by changing experimental parameters, such as the sublimation temperature of the ferrocene, the amount of growth promoters, the carbon source and its flow rate, and reaction temperature.^{56,59} **Fig. 2.6** shows some examples of shaped carbon nanomaterials that can be produced in different catalysed synthesis reactions.

Carbon nanomaterials such as SWCNTs and CNHs are characterised by large active surface area, good conductivity and chemical stability that have been used as a host material for the distribution of noble metal nanoparticles such as in in-situ growth of AuNPs on shaped carbon nanotubes or nanomaterials.⁶⁰ The ease of producing AuNPs of uniform dispersion and narrow size distribution is attributed to the pore structure of shaped carbon nanotubes or nanomaterials. A direct reduction route of depositing AuNPs on shaped carbon nanotubes or nanomaterials involves spontaneous reduction of AuNPs in organometallic complexes. This method has been used in the high yield catalytic synthesis of carbon nanomaterials. This method basically uses the CVD process of synthesis or more precisely FCCVD. The precursor organometallic complex used in one of the processes is ferrocene or iron pentacarbonyl (Fe(CO)₅) for the synthesis of shaped carbon nanomaterials.⁶¹

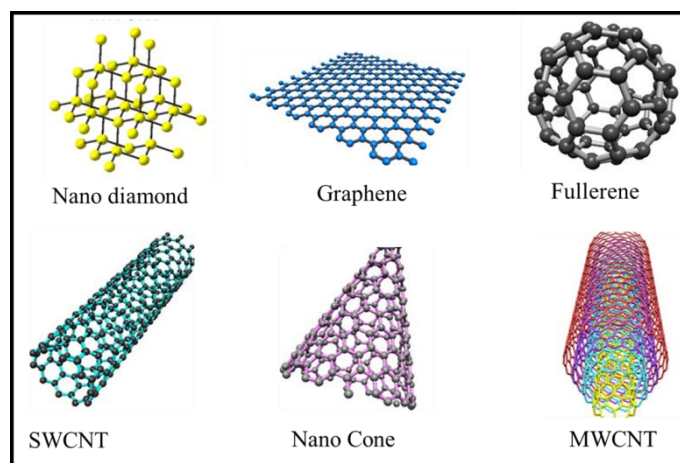


Figure 2.6 Structural representations of different types of carbon nanomaterials.⁶²

Shaped carbon nanotubes or nanomaterials have also been prepared from tailoring of carbon nanomaterials by irradiation-induced transformations. Amorphous C-films are irradiated in a JEOL 2010F field emission gun TEM to form shaped carbon nanotubes or nanomaterials. The electron beam carries a large current in a small area in the TEM. The electron beam is then condensed and is propagated to irradiate and open holes in a carbon film. It can form a thin graphitic bridge separating regions of carbon material formed. The beam is spread to soft irradiation conditions such that it reverts to normal current density observation values. The thin graphitic bridge is narrowed until forming shaped carbon nanotubes or nanomaterials.⁶³

The catalytic methods to make shaped carbon nanotubes or nanomaterials include catalytic decomposition of carbon precursor molecules such as hydrocarbons, CO or alcohols on the surface of transition metal nanoparticles. The shaped carbon nanotubes or nanomaterials can be produced via aerosol synthesis in a vertical laminar flow reactor.⁵⁵ The catalyst particles can be formed via nucleation and condensation of metal vapour, which is obtained by thermal decomposition of metal organic precursors such as ferrocene and iron and pentacarbonyl.⁶⁴

The set up for the catalyst particle formation via thermal decomposition of ferrocene included a saturator, a water-cooled injector probe, and a furnace. N_2 or CO carrier gas at a flow rate of $300 \text{ cm}^3 \text{ min}^{-1}$ was directed through the saturator filled with a mixture of silica and ferrocene powders. In another set-up, the introduction of iron pentacarbonyl vapour was done as above but the saturation of the carrier gas was by way of passing it through a liquid precursor reservoir. The metal-organic precursor vapours were introduced via the injector probe to a furnace set at a temperature at which iron pentacarbonyl precursor vapour immediately undergo decomposition forming iron vapour. The last set-up for catalyst particle

formation consisted of a hot wire generator (HWG) positioned inside the heated furnace and surrounded with a flow of mixed N_2/H_2 gas for protection. The metal vapour is formed via resistive heating.⁶⁴

Parametric studies were also done on the synthesis conditions in plasma-enhanced CVD for making high quality shaped carbon nanotubes or nanomaterials. This involved synthesis of shaped carbon nanotubes or nanomaterials from H_2/CH_4 mixtures on an MgO-supported mixed-metal Mo-Co catalyst using microwave plasma-enhanced chemical vapour deposition (PECVD) reactor.⁶⁵ The catalyst and support were prepared by wet mechanical mixing and a combustion synthesis procedure. The catalyst was prepared from a solution of molybdenum and cobalt nitrate hexahydrate and added to a solution containing $Mg(NO_3)_2$ and citric acid to make a mixed-metal Mo-Co catalyst on a nanoporous MgO-support.⁴³ The dispersed and dried catalyst was inserted into the PECVD reactor. Hydrogen gas was introduced into the chamber first, followed by methane thereby initiating the synthesis process. Various synthesis times and inlet gas flow rates were employed for the parametric study. The parametric study focused on the effect of synthesis temperature, inlet gas composition, synthesis time, and plasma power on the shaped carbon nanotubes or nanomaterials growth.⁶⁶ A similar study will be carried out in this work using La-Ni catalyst on mesoporous rutile TiO_2 RANR support as explained in details in **Chapter 9**.

Similar studies were carried out to determine the effect of FeO_x , CoO_x , and NiO catalysts and calcination temperatures on the synthesis of shaped carbon nanotubes or nanomaterials using a CVD method on a carbon source. These studies precede work done in this research as presented in **Chapters 5 – 7** of the results and discussion section. Previous studies reported on the use of CoO_x/Al_2O_3 catalyst in a synthesis carried out at atmospheric pressure in a fixed bed quartz reactor that was inserted into a stainless steel tube at a reaction temperature of 950 °C.^{67–69} The dried catalyst samples were calcined in air at 300, 600 and 850 °C and loaded into the reactor. The CCVD reaction was carried out for 30 min. The CoO_x/Al_2O_3 catalyst calcined at 300 °C produced ribbon-like and sheet-like shaped carbon nanotubes or nanomaterials. On increasing the calcination temperature to 600 °C, both MWCNTs and SWCNTs were formed. The FeO_x/Al_2O_3 catalyst calcined at 300 °C produced SWCNTs arranged in bundles which had smooth surfaces, which were long as well as straight. Calcining the catalyst at 600 °C produced shorter SWCNTs but of increased diameter of 4.03 nm as compared to 2.63 nm for the 300 °C calcined catalyst.⁶⁷

2.4 Photocatalysis studies

Nanotechnology has found wide uses in different industrial sectors including environmental water and waste water management, gas sensing and catalysis during photocatalysis, Fischer-Tropsch and other related applications. Nanotechnology is considered a key area in addressing the current drought, water shortage and water pollution challenges.⁷⁰ Nanotechnology has a potential of being designed into innovative, novel and cost-effective applications in environmental management including photo degradation of water and wastewater pollutants.⁷⁰ In this research, the prepared supported catalysts were tested for photocatalytic performance against pure RANR. Previous studies tested the photocatalytic degradation of a wide range of organic pollutants in water using pure TiO_2 and M/TiO_2 supported catalysts. The efficiency of TiO_2 as a photocatalyst is reported to be maximised by improving its charge carrier separation during the photo-electrochemical and photocatalytic processes. Noble supported metals such as Au and Pt are known to modify the TiO_2 and bring about improved charge carrier separation and plasmonic effects.²⁴

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Chapter 3

3.1 Methodology

3.1.1 Preparation of radially aligned nanorutile

A 250 ml round-bottomed flask filled with distilled water (100 ml) and fitted with a magnetic stirrer bar was placed in an ice-bath placed on a magnetic stirrer. A solution of TiCl_4 (12 ml) was added drop-wise to the flask while stirring. This solution was then heated under reflux at 200 °C for 24 h using an oil bath. The resulting precipitate was cooled to room temperature and centrifuged for 10 min at 3000 rpm and washed 3 times with using warm deionised water. The supernatant was transferred to a beaker and dried in an oven at 120 °C for 40 min.

3.1.2 Loading of metal catalysts on radially aligned nanorutile support

As discussed in Chapter 2, different authors have reported on a wide range of metal loadings onto various types of supports for diverse metal catalysts. Throughout this thesis, a common method of metal loading on the tips of the RANR was used for all the metal catalysts using DP urea method. The metals that were loaded on the RANR support were: Ni, Au, La and La-Ni.

3.1.3 Deposition-precipitation method using urea (DPU)

In each case a mass of 1 g of RANR was added to 100 ml of an aqueous solution containing a calculated concentration of precursor metal catalyst (4.2×10^{-3} M HAuCl_4), (0.408917g $\text{NiNO}_3 \cdot 6\text{H}_2\text{O}$), (0.14268g LaCl_3) and urea (0.42 M). The precursor metal compounds in the solution corresponded to 8 wt. %. Similar calculations were made for the other loadings, (0.5, 1, 2, 5 and 10 wt. %)The pH was initially set at approximately 2 using HCl. The suspension was refluxed at 70 °C and vigorously stirred for 24 to 72 h. This consequentially led to a gradual rise in pH from 2 to 9 as the urea decomposed. The solids thus formed were gathered by centrifugation at 3 000 rpm for 10 min. They were then washed in 100 ml distilled water under stirring for 10 min at 50 °C and then centrifuged. This washing step was repeated four times. The catalysts were dried at 60–70 °C for 2 h and stored in a dark cupboard under vacuum in a desiccator. The amount of gold in solution corresponded to a maximum metal loading on TiO_2 .

3.1.4 Chemical vapour deposition synthesis of carbon nanomaterials

A typical CVD set-up was used for the synthesis of the CNMs (**Fig. 3.1**). This set-up comprised a furnace fitted with a thermocouple and a temperature/time control panel. The furnace allowed for a quartz reactor tube to be inserted horizontally and was fitted with gas inlet and exit connectors. A weighed mass of each catalyst was placed into a quartz boat and then inserted into the centre of the quartz reactor tube. This was then placed into the furnace. Silicone inlet tubes that delivered acetylene (C_2H_2) and hydrogen (H_2) from the gas manifold were connected at the inlet connector to the quartz reactor tube. A silicone outlet tube was connected to a bubbler which exhausted to the exterior atmosphere (**Fig. 3.1**). The C_2H_2 served as the source of carbon in the synthesis of the CNMs and H_2 as a reducing agent and carrier gas. The synthesis of the CNMs was carried out by varying parametric conditions that were set for the reactions. The parameters that were varied were: temperature, reaction time, gas flow rate, catalyst wt. % loading and the type of catalyst used.

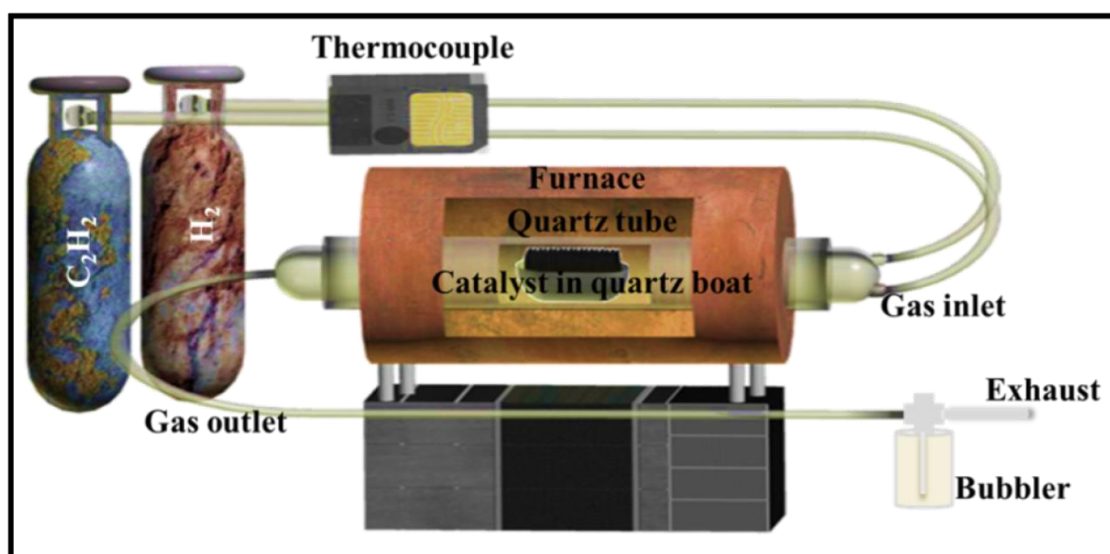


Figure 3.1: A diagram representing the CVD set-up that was used to synthesise SCNMs.

In each reaction 500 mg of catalyst was uniformly spread into a small quartz boat, and placed approximately at the centre of the furnace in a quartz reactor tube, to ensure controlled heating. A gas mixture of acetylene and hydrogen (C_2H_2/H_2) was then introduced into the reaction tube through the gas inlet and the exhaust was exited through the gas outlet. Gas mixtures comprising of C_2H_2/H_2 , with flow rates varying between $10 - 100 \text{ mL min}^{-1}$ and reaction temperatures ranging from $200 - 850 \text{ }^\circ\text{C}$ were set as reaction parameters for the

synthesis of the SCNMs. The furnace was heated to the desired temperature at rate of $10\text{ }^{\circ}\text{C min}^{-1}$, during which time H_2 was passed through the system. Once the desired temperature was reached, acetylene was then also allowed to pass through the quartz tube for a set period of time (30 – 120 min). Thereafter the acetylene flow was stopped, while the furnace cooled under a flow of H_2 . The as-synthesised material was then harvested for further characterisation.

3.1.5 Characterisation of RANR and supported catalysts

Detailed analyses of the RANR were carried out to determine their properties and characteristics, including the morphology of the RANR using powder X-ray diffraction (PXRD) and transmission electron microscopy (TEM). The precursor metal content of each sample was determined using thermogravimetric analysis (TGA). Samples of the respective catalysts were characterised using instrumentation presented and explained in **section 3.2**. Analyses using high resolution transmission electron microscopy (HRTEM), variable temperature powder X-ray diffraction (VTPXRD), Brunauer–Emmett–Teller (BET) surface area measurements, Fourier transform infra-red (FTIR) spectroscopy and TGA were used to provide detailed information in this regard. The RANR supported metal catalysts were then used in the synthesis of SCNMs.

3.2 Analyses

Samples of materials prepared and synthesised in this research were analysed and characterised using a wide range of instrumental techniques. The different techniques provided sets of data from which detailed interpretation revealed the intrinsic properties and characteristics of the materials. The catalyst nanoparticles were analysed using PXRD to determine the crystallographic phases and structures of the RANR support and the Au, Ni, La and La-Ni catalysts loaded on the support. PXRD was compared to electron probe microanalysis (EPMA) data. The wavelength dispersive spectra using wavelength dispersive spectroscopy (WDS) were used to map the distribution of elements in the sample by energy dispersive X-ray spectroscopy (EDS). Surface area studies were done using BET. Temperature programmed reduction/oxidation (TPR/O) analyses, both before and after the CVD reaction, revealed details of the behaviour of the RANR supported metal catalysts. TEM and scanning electron microscopy (SEM) were used to study the morphology of both the RANR supported catalysts and the SCNMs that were produced in these CVD reactions. The SCNMs were studied using laser Raman spectroscopy (LRS) and TGA to compare and

confirm the properties of these products. FTIR spectroscopy was used to analyse the bonding in the RANR supported metal catalysts and to understand their chemical interaction and the SCNMs that were produced. The RANR and the supported Au, Ni, La and La-Ni catalysts were further tested for photo degradation of methyl orange (MeO) by irradiating the sample with simulated sunlight generated by a Newport illuminator solar simulator. The degradation reaction of MeO was monitored using a UV/vis spectrophotometer.

3.2.1 Powder X-ray diffraction (PXRD)

The fundamental use of PXRD is in the identification of components in a sample. This technique operates under the premise that about 95 % of all solid materials (organic and inorganic) can be described as crystalline and are capable of interacting with X-rays to give a diffraction pattern.¹ Every crystalline substance gives a pattern and will always give the same pattern even in a mixture of substances.² The area under the peak of a given phase of that substance gives a measure of the quantity of that phase present in the sample. The X-ray diffraction pattern of a pure substance is essentially like a fingerprint of the substance thus PXRD can distinctively identify and characterise polycrystalline phases. The fingerprint PXRD pattern is derived from the diffraction of X-rays by atoms arranged in a certain sequence that make up the crystalline form of the solid material. The disorderliness and random arrangement of atoms in a material gives rise to materials described as amorphous solids. Regularly arranged atoms in systematic sequential repetitions in three dimensions describes solid crystals and hence crystallinity. The smallest volume of a crystal is a unit cell.

In this work, samples were analysed using a Bruker D2 Phaser PXRD (**Fig. 3.2**) that used Co-K α radiation which made use of a 30 kV X-ray tube and a current of 30 mA over a $10^\circ \leq 2\theta \leq 90^\circ$ range. The diffractometer made use of the Bragg – Brentano geometry with an incident angle defined between the X-ray source and the sample while the diffraction angle 2θ , was defined between the incident beam and the detector.¹ However, the diffraction vector was always normal to the surface of the sample. Careful sample preparation was required. Here packing of the sample into a sample holder to gain an almost flat plane surface that could be further pressed with a glass plate to attain a smoothened surface with a uniform height was required (**Fig. 3.3**). Both calcined and non-calcined samples were prepared in this way for control purposes and tracking phase transitions during calcination.

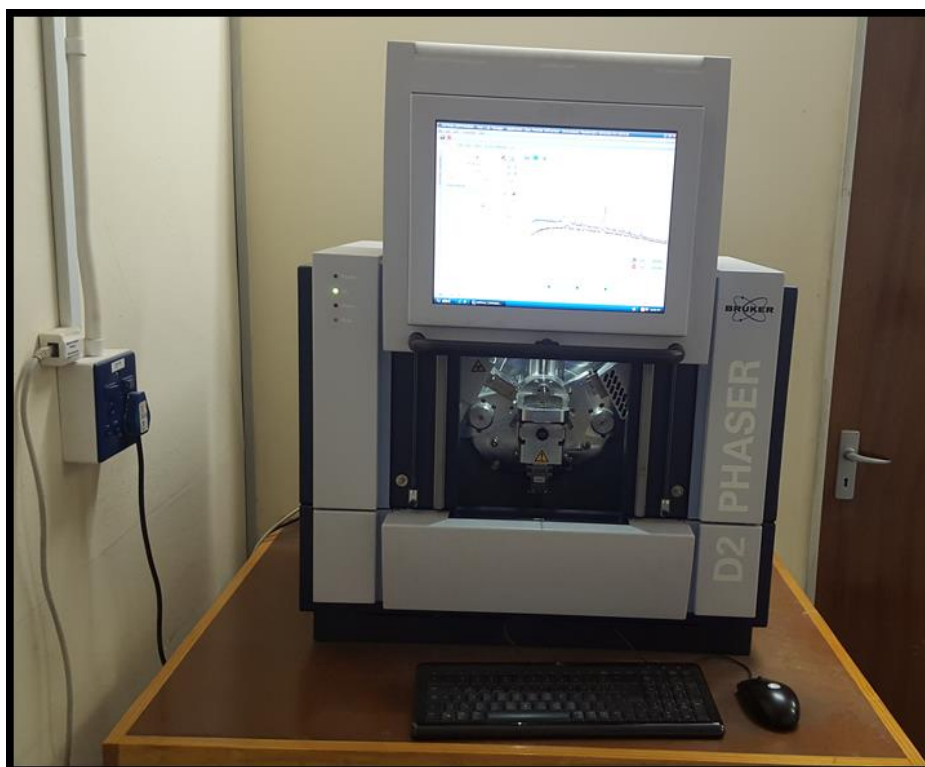


Figure 3.2: The Bruker D2 Phaser PXRD fitted with a LynxEye detector.



Figure 3.3: Sample preparation for PXRD analysis.

Scans were measured over a 30 min period with sample rotation during scanning. The scans produced a set of data which include peak patterns, lattice parameters and Miller indices. The

peak patterns were identified by searching through an inorganic crystal structure database (ICSD) that matched phases which occurred at their respective 2θ values using EVA software.

3.2.2 Electron probe microanalysis (EPMA)

EPMA is a technique which identifies and measures concentrations of elements in microscopic volumes of a sample using X-ray spectroscopy. The operating technique makes use of an electron beam focused on a sample and interacts with it to generate an array of four different types of electrons. The electron beam may be back-scattered to give back-scattered electrons (BSE), secondary electrons (SE), characteristic X-rays and cathodoluminescence light (CL).³ The surface scans of the sample, using the electron beam, produces signals that can be used to acquire X-ray maps, high resolution scanning electron images, phase identification images from the CL data, phase distribution, estimation of proportions, elemental composition variation and surface textural analysis of multi-phased composites.³ Quantitative chemical analysis can also be carried out using the characteristic X-rays of various substances. The technical application of EPMA combines both energy dispersive and five wavelength dispersive spectrometers (EDS and WDS) at the microprobes to perform quantitative and qualitative analyses. EPMA uses high sensitivity crystals that allow a 3-fold increase in count rate, while maintaining good peak to background ratio and spectral resolution. The microprobes are operated at a high vacuum in the pressure range of 2×10^{-5} - 10^{-6} .⁴

EPMA analyses in this research were performed with a CAMECA SX5-FE-EPMA (**Fig. 3.4**) which was operated at 15 kV and at a working current of 20 mA. EPMA was used to analyse the RANR supported metal catalysts, both mono (La, Ni and Au) and mixed-metal (La-Ni) loaded, for their elemental distribution by WDS mapping and quantitative analysis by characteristic X-rays. The spatial distributions were also determined by X-ray maps.



Figure 3.4: The electron probe micro-analysis assembly.

3.2.3 Scanning electron microscopy (SEM)

SEM is a technique that is used for achieving high resolution images of surfaces. It involves scanning a fine beam of electrons over a specimen and detecting the signals which are emitted. Scanning electron microscopy permits electron beam excitation of the sample that generates signals detectable on the cathode ray tube-types of detectors that visualise and record the sample image. The visual images of the sample can be generated from signals due to the displaying of: secondary electrons, back-scattered electrons, transmitted electrons or sample current.⁵ The secondary electron image is formed by both the secondary electrons and the back-scattered electrons that reach the detector. This is because the secondary electrons are generated from within a few nm from the surface of the sample. The resolution of modern SEM instruments is of the order of 2 nm. Thus they are very sensitive to surface structure, and provide topographical information. On the other hand, the back-scattered electrons are generated from deep within the sample and interact much more strongly with the sample. They thus provide compositional information.

A FEI Nova Nanolab 600 FEG-SEM, operated at 30 kV with a spot size of 0.63 nA, was used in this research work (**Fig 3.5**). The La, Au, Ni and La-Ni nanoparticles supported on RANR were analysed in a detailed study of morphological structure before and after use in the CVD

synthesis of SCNMs. The as-synthesised SCNMs were also characterised under SEM and EDS to determine the elemental composition of the catalyst – SCNM system.

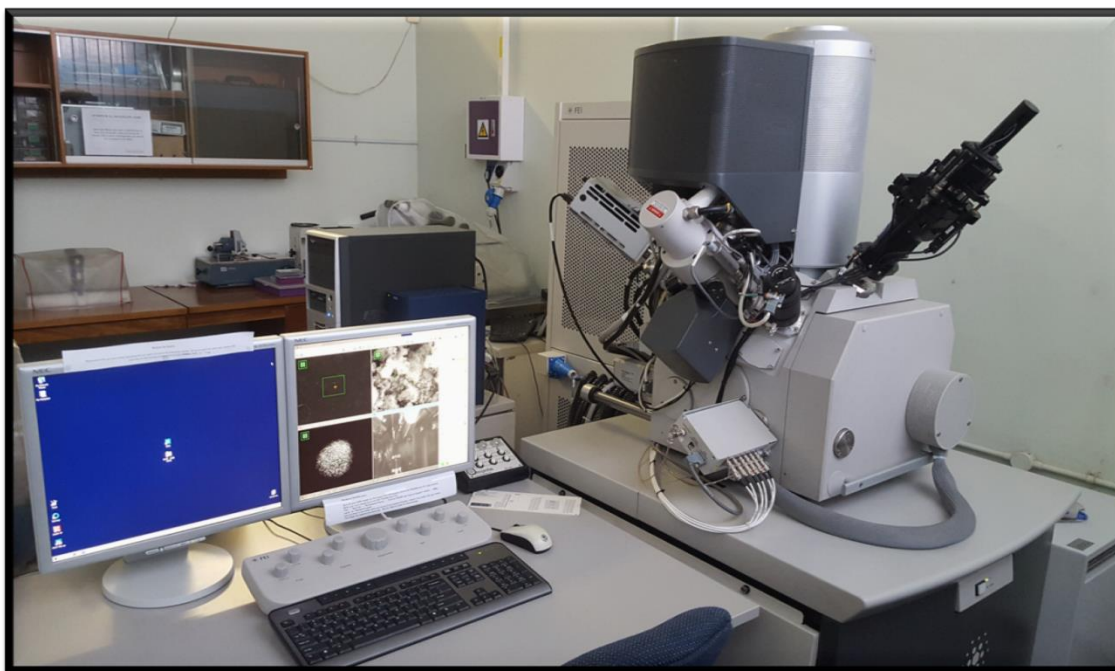


Figure 3.5:The FEI Nova Nanolab 600 FEG-SEM/FIB.

3.2.4 Transmission electron microscopy (TEM)

TEM is able to generate high resolution images of samples at magnifications as high as 0.5 nm from a high powered beam of electrons accelerated at 120 kV.⁶ These electrons are generated from thermionic or field emission sources after which a series of lenses facilitate their collection and focus into the optical path. It is the optical quality of the lenses that control the resolution of the electron microscope.⁷ However, these lenses are affected by factors such as: astigmatism as well as spherical and chromatic aberration.

The mechanism of TEM imaging involves manipulating the beam of electrons using condenser lenses that focuses the electron beam onto the sample surface as shown in **Fig. 3.6**. The beam-surface interaction results in different types of scattering and parts of it are transmitted. These transmitted electrons are focused by the objective lens into an image on the charge-coupled device (CCD) camera.⁸ The image is enhanced in its contrast using objective apertures and is enlarged as the image is propagated down the column through the intermediate and projector lenses.

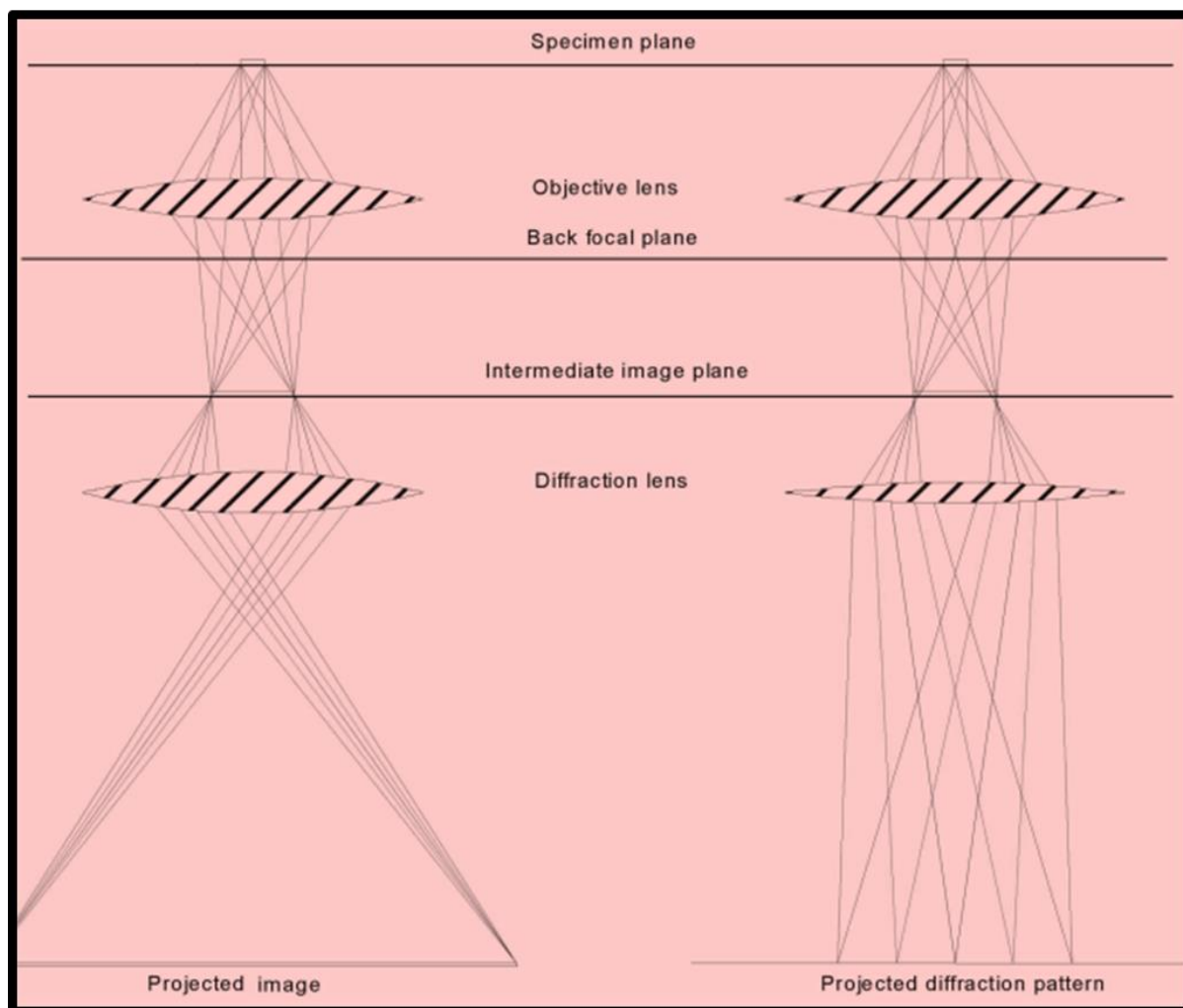


Figure 3.6 Beam geometries in the TEM for imaging (on the left) and diffraction (on the right) modes.⁹

Parameters such as morphology, crystal structure of materials, phase transitions, grain arrangement, particle size and diameter measurements are able to be determined by TEM analysis.⁷ The use of TEM also enables the revelation of the finest details of internal structure. Similarly extrapolations of TEM data from a series of reaction products can be used to determine a step-by-step mechanism of the reaction process.⁷

In this work, a FEI Tecnai T12 transmission electron microscope (**Fig. 3.7**) was used to characterise the morphological properties and characteristics of both the RANR supported metal catalysts as well as the SCNMs that were synthesised via the CVD method.

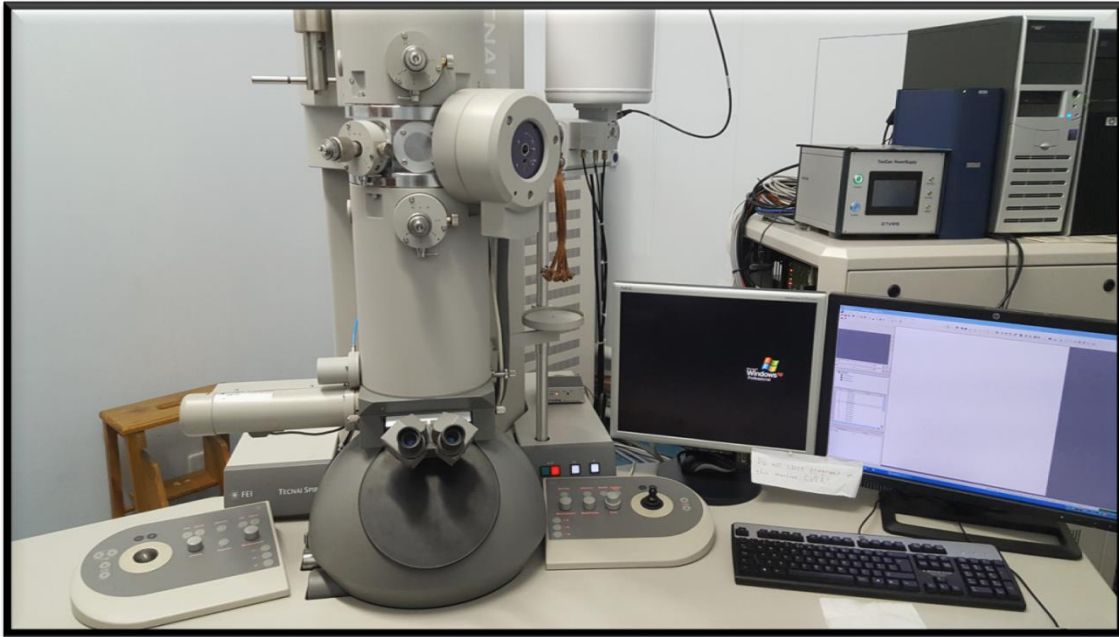


Figure 3.7: The FEI TECNAI T12 transmission electron microscope.

3.2.5 Energy dispersive X-ray spectroscopy (EDS)

EDS analysis is a technique that scans the X-rays generated from the interaction of an electron beam with a sample. Because some of the X-rays produced in this manner have wavelengths and energies that are characteristic of the elements therein, this allows their distribution and the sample's composition to be determined.⁶ EDS is specifically useful in acquiring rapid qualitative analysis of an unknown sample. EDS is also used to complement broader analyses such as TEM, SEM, and EPMA-WDS. Therefore these previously mentioned instruments are used to perform EDS. EDS relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing a unique set of peaks on its electromagnetic emission spectrum. To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons, or a beam of X-rays, is focused into the sample being studied. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer.

3.2.6 Temperature programmed reduction/oxidation (TPR/TPO)

TPR analyses provide fundamental information in catalysis in terms of the chemical stability of the material being analysed, both in a free or controlled atmospheric environment. TPR or TPO analyses are performed in order to find the most efficient reduction or oxidation conditions. TPR/TPO is also useful for identifying the supported precursor phases and their interactions with the support.¹⁰ Consequently the data obtained from TPR/TPO can be used to predict the conditions under which the supported catalysts may be used, while still retaining their distinct physical and chemical characteristics. Ideally, the support material should reduce or oxidise at a higher temperature than the catalysts it supports. TPR is also used as a characterisation of complex systems such as mixed-metal or doped catalysts and to determine the role of the second component and to establish the formation of alloys or promotion effects.¹¹

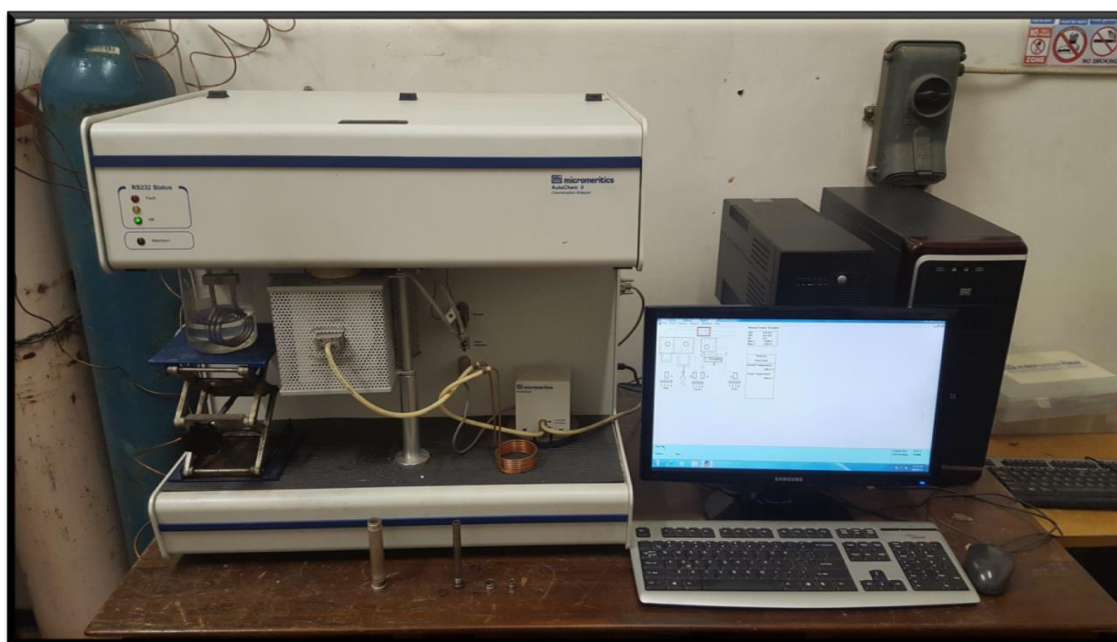


Figure 3.8 Micromeritics RS232 TPR/TPO analyser.

In this research Au, La, Ni and La-Ni catalysts were supported on RANR. TPR analyses were performed on these materials using a Micromeritics Autochem II chemisorption analyser, model RS232 Status. A typical TPR analysis involved placing a precursor metal oxide catalyst (such as Au_2O_3 , NiO , La_2O_3 and $\text{La}_2\text{O}_3\text{-NiO}$) supported on RANR into the Micromeritics analyser (**Fig. 3.8**). This was then set to a reduction temperature range ramped at $10\text{ }^\circ\text{C min}^{-1}$ while a reducing gas mixture (H_2/Ar) flowed over each supported catalyst.

Reduction rates were measured by the change in composition of the expended gas. In this way the H₂ concentration decrease in the expended gas, as compared to its initial concentration was measured.¹² This provided useful quantitative and qualitative information on the reactivity as well as the behaviour of the supported catalysts, and made it possible to set conditions for optimizing the reactions to be catalysed as well as predicting other parameters of the reaction. In this research, the TPR data was further used to determine catalyst co-loading of catalysts on the support.

3.2.7 BET surface area analysis (BET)

Specific surface area (SSA) is a measure of the total surface area of a material per unit of mass of that material. SSA is therefore measured in m² kg⁻¹ or m² g⁻¹ and is used to determine the characteristic properties of a material. This fundamental information, obtained from BET analysis, has important implications for adsorption, heterogeneous catalysis and reaction surfaces. SSA may be determined using different measurement methods such as by: i) simple calculation from the particle size distribution, ii) adsorption measurements by BET isotherms, and iii) gas permeability.¹³ However, all these methods except for BET, fail to measure much of the surface, fine structure and deep texture of the particles. However, BET measurements may greatly differ due to the substance used in the adsorption process. BET surface area analyses make use of nitrogen gas being adsorbed on the surfaces of powdered solids, where the volumes adsorbed are measured at a constant temperature i.e. 77.4 K and the lowest relative pressure.¹⁴



Figure 3.9 Micromeritics RS232 Brunauer -Emmett-Teller (BET) surface area analyser.

In this research, a Micromeritics RS232 BET surface analyser (**Fig. 3.9**) was used to determine the specific surface area of the novel support material i.e. RANR, in an attempt to understand the topology of the nanorods onto which the metal catalyst nanoparticles were loaded. Surface area studies were performed on these supported RANR catalysts in an attempt to understand their reaction kinetics.

3.2.8 Fourier transform infra-red (FTIR) spectroscopy

Materials absorb light in different regions of the spectrum in distinct ways. However, most materials absorb in the infrared region. These absorptions result in changes in the vibrational and rotational modes of the molecules in these materials, due to a change in their dipole moments. Consequently, the absorption frequencies of a material are determined by the vibrational frequencies of the molecules (of which it is made), which in turn influence the infrared photon energy transfer efficiency.¹⁵ Here, a measure of the magnitude of the infrared photon energy transfer gives the absorption intensity.



Figure 3.10 Bruker Tensor 27 FTIR analyser.

Compared to other infrared spectroscopies, FTIR spectroscopy is useful in the quantification of several components absorbing in the mid-infrared region. This is because FTIR analysis has a better signal-to-noise ratio than other methods such as HPLC and UV-vis. The technical innovation involved in FTIR is the use of an interferometer instead of a monochromator and slits. The operation mechanism is characterised by the splitting of a beam into two different

paths. Once the beams are allowed to recombine after interference, the intensity of the output beam is monitored as a function of path difference by using a detector.¹⁶

In this research, a Bruker Tensor 27 FTIR analyser (**Fig. 3.10**) was used to monitor the growth of RANR. Thereafter this analysis was extended to RANR supported catalysts to determine the extent of interaction at the metal catalyst – support interface. These analyses generated spectra that served as unique molecular fingerprints that were easily distinguished from the absorption patterns of other molecules.

3.2.9 Laser Raman spectroscopy

Laser Raman spectral analysis is a technique that characterises materials with unique vibrational and crystallographic information that is derived from electronic states and phonon energy dispersion in an electrochemical system of a material.¹⁷ This information enables detailed studies of the physical properties that are relevant to electrons and phonons. LRS is commonly used to characterise sp^2 carbons such as: 3D graphite, 2D graphene, 1D carbon nanotubes and 0D fullerenes.¹⁸

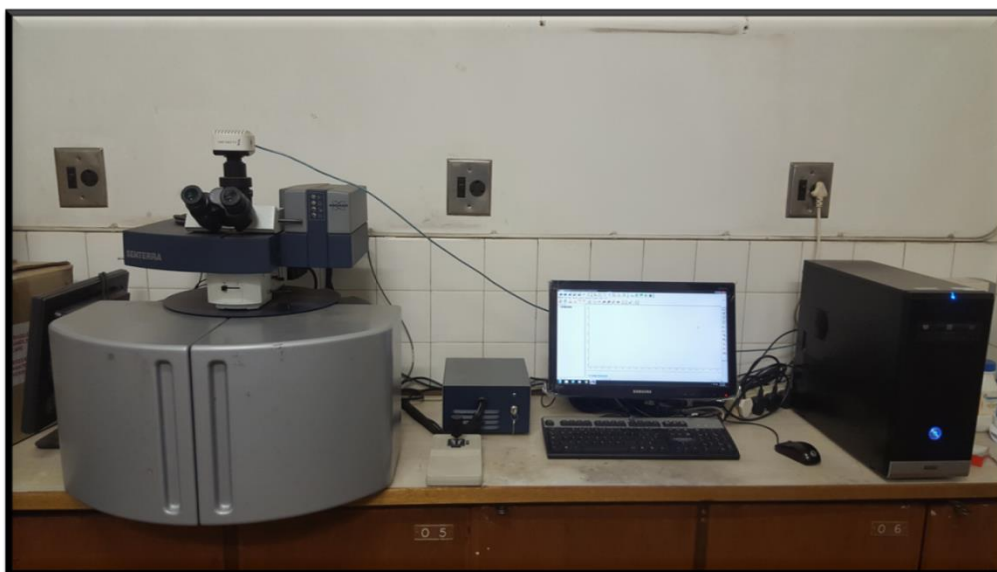


Figure 3.11 Bruker Senterra Laser Raman Spectrometer.

Structural characterisation of graphitic materials provides particularly valuable information about defects, stacking of the graphene layers and the finite sizes of the crystallites parallel and perpendicular to the hexagonal axis. LRS is a comparatively easy, non-destructive, non-contacting and rapid measurement method to examine the inelastic scattering of light from a

sample surface at room temperature and ambient pressure. The Raman spectra of graphitic materials are commonly characterised by two dominant spectral features, the G and G' bands appearing at 1582 cm^{-1} and 2700 cm^{-1} , as well as the D and D' bands occurring at 1350 cm^{-1} and 1620 cm^{-1} respectively.¹⁹ The D-band feature stems from the disorder-induced mode. It has a second harmonic called G' –band. Measurements of the D-band and the G'–band frequencies at the single nanotube level therefore provide unique information on the chirality and diameter dependence of D and G' that can be used to determine the magnitude of the trigonal warping effect in the electron and phonon dispersion relations.¹⁹

The laser Raman spectrometer used in this research was a Bruker Senterra (**Fig. 3.11**) fitted with a 50x objective lens for imaging. Here the laser excitation wavelength was set to 532 nm and spectral data were evaluated using OPUS 7.1 software. Detailed studies were carried out on the CVD products synthesised over the various supported catalysts (Au, La, Ni and La-Ni/RANR), under different sets of parametric conditions. These studies were conducted to determine the effect of varying the parametric conditions of synthesis in terms of graphicity and crystallinity of the products.

3.2.10 Thermogravimetric analysis (TGA)

The basis of TGA is the monitoring of the mass of a material as a function of temperature or time under a controlled temperature and atmosphere. This involves heating a material and measuring its weight as it is heated or cooled in a furnace. The material is loaded on a specialised pan supported by a precision balance that measures its mass loss/gain against temperature or time. These measurements can quantify the extent of water, solvent and plasticizer loss, decarboxylation, pyrolysis, oxidation, decomposition, wt. % filler, catalytic metal residue (remaining in SCNMs) as well as wt. % ash.²⁰

In this research TGA was applied in the characterisation of the SCNMs that were synthesised via CVD over Au, La, Ni and La-Ni metal nanoparticle catalysts deposited on novel RANR supports. Here TGA was used to determine the mass of catalytic metal residue that remained on these SCNMs as well as the composition of the supported catalysts and their CVD products as well as their thermal stabilities. The decomposition temperature information gained this way was useful in distinguishing the degree of crystallinity in the different carbonaceous materials and was used to complement the PXRD and Raman data that were obtained. In this research a Perkin Elmer TGA Simultaneous analyser STA 6000 Pyris Series (**Fig. 3.12**) was used for the TGA analyses.



Figure 3.12 TGA – MS Simultaneous Thermal analyser.

3.2.11 Ultraviolet–visible spectroscopy (UV-vis)

Modern chemistry has seen wide applications of spectroscopic methods in the identification of molecular structures. UV-vis spectroscopy has been used to determine molecular structures, sizes of nanoparticles,²¹ concentrations of solution, confirmation of molecular structures, monitoring progress of reactions and to control the purity of compounds. The UV-vis spectrophotometer comprises five main components in its assembly.²² The first is a light source such as a hollow cathode lamp, deuterium lamp or a tungsten lamp. This is used to generate light in the UV, visible or infrared spectral ranges. The second is a monochromator which is used to select light frequency with uniform wavelength from the lamp. The third is a specialised sample holding compartment in which the fourth component fit, i.e. the cuvettes which contain the sample and allow light to pass through them. Finally the intensity of the light of each monochromatic beam after passing through the sample is measured by the detector or photomultiplier in the UV-vis spectral range.



Figure 3.13 Varian UV-vis spectrophotometer.

The spectral scans and the adsorption spectra are then displayed on a computer. In this research the Varian UV-vis 50 Conc. spectrophotometer (**Fig. 3.13**) was used to monitor the photodegradation of methyl orange (MeO) by using different RANR supported catalysts at an uniform wt. % loading. In these studies, the photodegradation of MeO was initiated using light originating from a Newport illuminator solar simulator (see section 3.2.12) using a range of parameters including volume, amount of supported catalyst, catalyst type and duration of degradation. Here reactions were monitored by measuring the MeO concentration changes in the MeO/catalyst mixture under illumination at a constant stir rate with samples drawn at regular time intervals. The adsorption spectra of the MeO at time (t) were then represented on a computer display.²³

3.2.12 Solar simulator

Solar simulators are designed to imitate the directional, spatial and spectral distributions of concentrated solar radiation that is acquired at the focal plane of a highly concentrating system. In this research an Oriel instrument 50 – 500 W power input Newport illuminator solar simulator WX00048 (**Fig. 3.14**). The solar simulator comprised three main components: i) the power supply, ii) the digital exposure control and iii) a reflector adjustor with horizontal and vertical lamps.



Figure 3.14 Newport Illuminator Solar Simulator Oriel Instruments WX00048.

The radiation source was a high powered lamp that delivers a continuous beam of intense thermal radiation.²⁴ The arc lamp produce different kinds of radiation at visible wavelengths with additional power in the infrared and ultraviolet regions of the spectrum.²⁵ Their spectral distributions are then adjusted using a reflector adjuster by altering the horizontal and vertical lamps to closely match the sun's real output. Here the reflectance may be expressed as a Kubelka–Munk algorithmic equation:²⁵

$$K = \frac{(1 - R)^2}{2R} = F(R)$$

Where: K = reflectance transformed

R = percentage reflectance

$F(R)$ = Kubelka-Munk remission function

In such cases a high power linear arc of 200 kW electrical output may deliver as much as 75 kW of continuous radiative power at its focal plane with peak fluxes of 4250 suns.

Where $1 \text{ sun} = 1 \text{ kW m}^{-2}$.

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Chapter 4

Au, Ni and La metal nanoparticles supported on RANR

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4.1 Introduction

The advent of catalysis for chemical reactions has seen the use of many different types of metals as catalysts. Detailed studies have identified metals that perform best as catalysts while other metal oxides as catalyst support.¹ Materials such as alumina, silica, lanthanum oxide and other transition metal oxides are often used as catalyst supports.² The choice of the support material is influenced by their properties and characteristics and how they enhance the behaviour and performance of the metal catalysts they support.² Different materials have alternate morphologies on which catalyst nanoparticles can be supported due to the various ways in which they crystallise.³ Some branches of research focus on methods to fabricate a support material that allows small nanoparticle catalysts to be loaded with required properties and characteristics.⁴⁻⁶

RANR have been prepared for use in photocatalytic reactions.⁷ In the work presented here, the RANR morphology was explored as a support for Au, Ni La and co-loaded La-Ni metal nanoparticles. Detailed studies were carried out to determine how the RANR structure supported metal nanoparticles. The choice of the metals was carefully done considering their positions on the periodic table. Ni is known to catalyse the synthesis of CNMs. Its behaviour was tested on the unique RANR support and compared to a higher transition metal, Au. Further testing was taken to a different metal group, La and effect of co-loading tested on La-Ni lanthanide-transition system.

4.2 Literature review

Transition metal oxides have been used extensively to support metal nanoparticles for use as catalysts.¹ Synthesis of TiO₂ (titania) support nanostructures in various morphologies has been widely researched due to their application as photocatalysts. The efficiency of a catalyst is strongly dependent on the particle size, crystalline phase, extent of crystallinity, surface properties and the particle and support morphology.⁸ For instance, microspheres assembled with nanorods have been found to exhibit low reflectance and also have efficient light harvesting properties due to the ordered nanorod units.⁹

Hierarchical porous nanostructures with macropores in combination with mesopores or micropores are of particular significance in practical applications. Such a multi-scaled pore system has advantages over unimodal pore size materials in terms of diffusion efficiency, accessibility to the pores by guest species, and large pore volumes.¹⁰ Macropores allow large guest molecules to access and achieve an efficient mass transport through the porous structures. The micropores or mesopores enhance the selectivity and the surface area of the nanostructures.¹¹ Porous channels of hierarchical porous structured photocatalysts are selective for the reactants or product and increase the adsorptive sites and reactive channels for in situ reactions. They are convenient for electron flow and most importantly macroporosity and mesoporosity are favourable for light propagation and photon absorption that could effectively enhance photocatalytic reaction efficiency.¹²

Titania has been used as a photocatalyst for the removal of hazardous organic substances; a nanostructured reservoir for corrosion-resistant coatings; nanorod films for studying reversible super hydrophobicity behaviour; an electrode material for dye-sensitized solar cells and lithium batteries; a component in mesoporous membranes for ultrafiltration; and as an additive for fuel cell membranes.⁵⁻⁷

Titania has three naturally occurring polymorphs: brookite (orthorhombic), anatase (tetragonal), and rutile (tetragonal). Rutile is the thermodynamically favoured phase, whereas anatase and brookite are both metastable to rutile at all temperatures. It has been widely demonstrated that some properties (such as crystalline phase and surface activity) of titania are very sensitive to its microstructure.¹³

Hydrothermal synthesis has been used in the preparation of titania nanostructures with tuneable phase and shape.¹⁴ Using hydrothermal preparation of titania at temperatures of 200 °C, pure rutile phase has been obtained.¹⁵ Rutile phase titania has been shown to be attractive for many applications largely because of its thermal stability and optical properties.

The time evolution of titania rutile growth indicates a three-step growth process for the formation of RANR. At the very beginning, TiO₂ anatase nanoparticles precipitate in the solution as a result of homogeneous nucleation.¹⁶ As reaction time proceeds, the particles aggregate and grow through a redissolution mechanism to form nanorods. The rods grow along the [001] direction due to the presence of a high-energy surface leading to loosely packed immature radially aligned nanorods. In time, further deposition and in situ annealing lead to densely packed mature dandelions.⁸ The nanorods, which can form the mature dandelions, are not uniform and continuous along the entire radius of the dandelions.¹⁷

Gold in the form of nanoparticles supported on transition metal oxides has found application as a catalyst effective at low reaction temperatures for the oxidation of CO and the decomposition of trimethylamine amongst many other applications.^{18,19} Nano-scale Au particle size gives it catalytic activity, as opposed to the inert bulk gold. Bulk Ni and La metals also have low catalytic activity, while in the nano-form they are highly active. This is generally explained by the absence of partially filled d-orbitals which make the metallic catalysts unable to chemisorb small molecules.²⁰ Previous studies revealed that nano-Au deposited on transition metal oxides such as Fe₂O₃, TiO₂ and Co₃O₄ is very active for room temperature oxidation of CO.²¹ Of particular interest for this work, however, is the potential of mutual stabilisation of the titania substrate and the metal nanoparticles for application in the growth of carbon nanomaterials.¹⁹

4.3 Experimental

4.3.1 Preparation of RANR

A 250 ml round-bottomed flask filled with distilled water (100 ml) and fitted with a magnetic stirrer bar was placed in an ice-bath placed on a magnetic heater stirrer. TiCl_4 (Sigma Aldrich CAS number 7550-45-0, 12 ml) was added drop-wise to the flask while stirring vigorously. This solution was then refluxed at 200°C for 24 h while stirring. The resulting precipitate was cooled to room temperature and centrifuged for 10 minutes at 3000 rpm and washed 3 times with 100 ml warm distilled water. The precipitate was transferred to a beaker and dried in an oven at 120°C for 40 minutes.

4.3.2 Deposition-precipitation method using urea (DPU)

The DPU method to make metal catalysts was used to make Au/TiO_2 described in previous studies.^{19,22} A determined amount of precursor metal salt was added to 1 g of RANR in 100 ml of water in a round bottomed flask. A stoichiometric excess of 100 times the metal concentration of urea was then added to the mixture and this was vigorously stirred while heating to 80°C to obtain the desired metal loadings ranging from 0.5 to 10 wt. %. Hydrated chloroauric acid ($\text{HAuCl}_4 \cdot 6\text{H}_2\text{O}$, SA Precious Metals) was used as the gold source, solid LaCl_3 (Sigma Aldrich CAS number 10099–58–8) was the source of La and nickel (II) acetate tetrahydrate ($\text{Ni}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$) (Sigma Aldrich) as the Ni source. The purpose of the use of urea was because urea decomposes slowly meaning that there is no sudden increase in pH in a localised region of the solution as observed with the addition of hydroxyl species. In aqueous conditions, urea hydrolyzes upon heating above 60°C and precipitates metal ions from solution and deposits them on the support material (RANR).

The DPU was carried out over a 24 h period. This is because the longer the deposition time, the higher the nanoparticle distribution. The gradual decomposition of urea over time facilitated the breaking down of the metal nanoparticles into smallest particle size possible. The solid material was gathered by centrifugation at 3 000 rpm for 10 min. After washing with 100 ml distilled water while stirring for 10 min at 50°C , the solids were collected by centrifugation. This washing step was repeated four times. The supported catalysts were dried at $60\text{--}70^\circ\text{C}$ for 2 h and stored in dark cupboard under vacuum in a desiccator.^{22,23} The

prepared catalysts were calcined at 700 °C for 4 h and reduced at different temperatures as explained in **Section 4.4.6**.

4.3.3 Characterisation techniques

Detailed morphological analyses of the RANR and the RANR supported metal nanoparticles were performed using scanning electron microscopy (SEM, FEI Nova FIB) and transmission electron microscopy (TEM, FEI Spirit 120 kV). The average particle size was determined using manual measurement tools in ImageJ on TEM and SEM images. A minimum of 200 particles were counted on the images. The crystallographic phases of the RANR and the supported nanoparticles were determined using powder X-ray diffraction (PXRD) on a Bruker D2 Phaser diffractometer in a 2θ range from 7° to 120° using Co K α radiation.

BET (Micromeritics Tristar–Surface area and Porosity Analyser 3000) measurements were performed to determine surface area, pore-volume and pore size of the RANR and metal loaded RANR. Sample material (200 mg), was degassed at 150 °C for 4 h under N₂ to remove the moisture before the BET analysis.

Hydrogen temperature programmed reduction (H₂-TPR) analysis of the dried and calcined metal loaded RANR was performed on a TPR-Micromeritics AutoChem II Chemisorption Analyser 2920 Status unit. The unit is equipped with a thermal conductivity detector to determine the optimum temperatures at which the metal oxides reduce. In the TPR analysis, 100 mg of catalyst sample was placed in a U-shaped quartz sample tube. Prior to TPR analysis, each sample was pre-treated under flowing Ar at 150 °C for 30 min. After the pre-treatment, the sample was cooled to room temperature. The gas flow was then switched to 5% H₂ in Ar balance at 50 ml min⁻¹ and the sample was heated to 900 °C at a constant rate of 10 °C/min. A thermocouple in the furnace of the sample compartment monitored the temperature during the ramping and cooling process.

4.4 Results and discussion

4.4.1 Structure and morphology of RANR

RANR particles were successfully synthesised reproducibly in a series of reactions to make as much RANR as possible. More than 20 pots of RANR synthesis were set up throughout this research work. TEM images of the as-synthesised RANR are shown in **Fig. 4.1**. The images of an enlarged individual RANR particle are shown in **Fig. 4.1(c)**. The mean diameter of the nanorods was 2-12 nm and lengths ranged from 50–650 nm. The nanorods were densely packed and spherically aligned. Previous studies suggested that the growth pattern of the nanorods is along the 110 axis of the rutile crystal plane with a preferred orientation in the 001 direction.^{24, 25}

Fig. 4.2 shows typical 3D SEM images of the as-prepared RANR. Magnified views of individual RANR particles are shown in images (b) and (c) of **Fig. 4.2**. The images show the RANR at various stages of formation brought about by the parameters of the hydrothermal method of synthesis. These parameters include reaction time, reaction temperature, reactant concentrations, as well as the solution's pH value as reported by Bai X *et al.*¹⁶ The reaction parameters are critical in the hydrothermal synthesis of RANR nanostructures. J. Zhou *et al.* illustrated the growth mechanism of the 3D dandelion-like nanostructures under various experimental conditions.²⁶ Here we observed that reaction parameters directly influenced the degree of nucleation of TiO₂ in the formation of 3D RANR nanostructures. Therefore reproducibility depended on how the optimum conditions were set.

The PXRD pattern of RANR in **Fig. 4.3** confirms the material to be a pure phase of rutile TiO₂. The pattern shows anisotropy of the peak shapes for different crystallographic planes, consistent with a material composed of nanorods that have all grown along a single plane during the formation of the RANR structure.

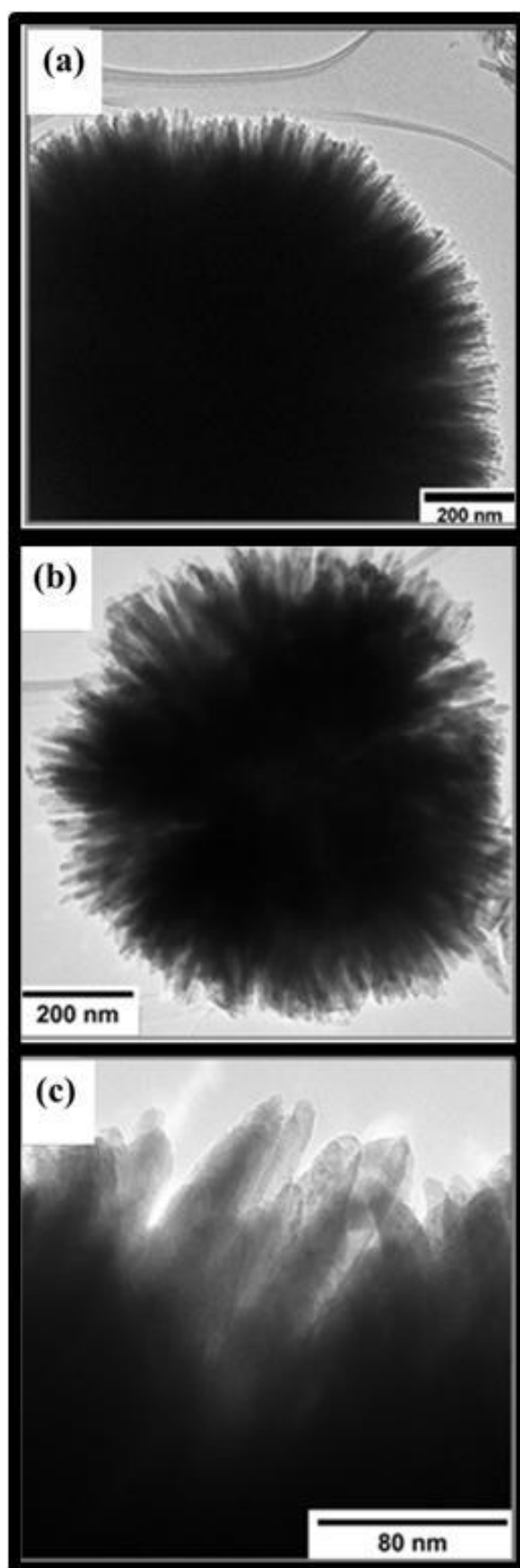


Figure 4.1 TEM images of RANR showing the radial alignment of the rods (a) and (b) and the termination of the tips (c).

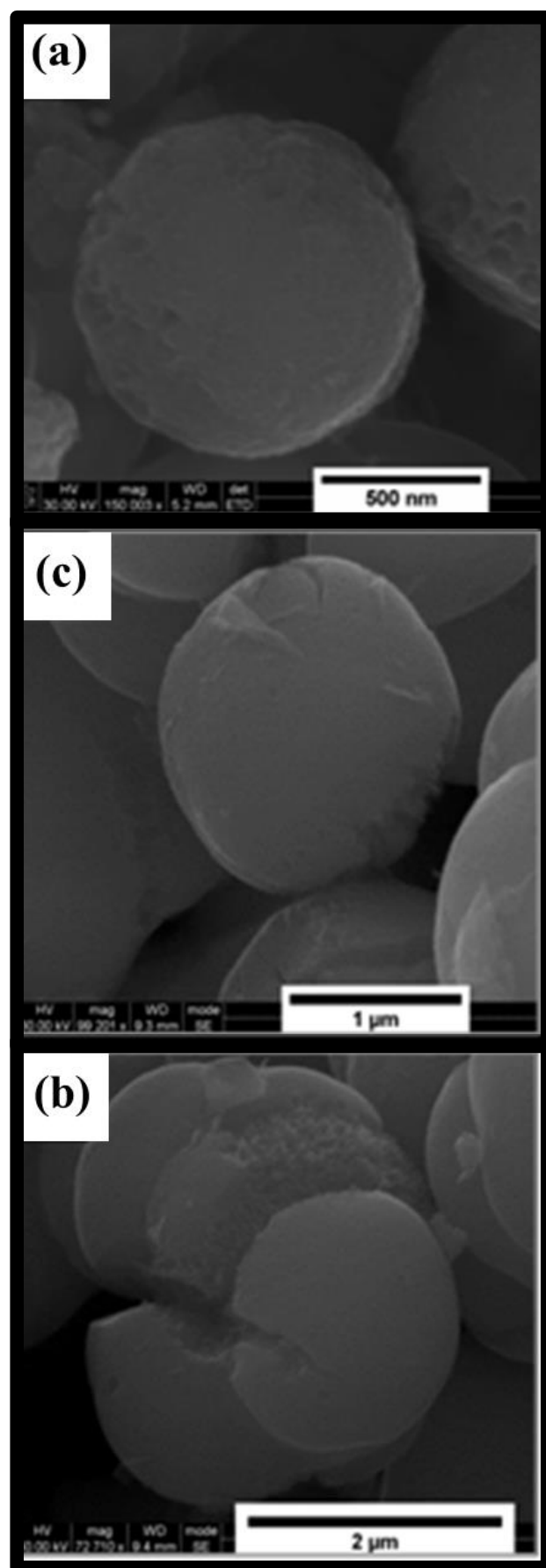


Figure 4.2 SEM images of RANR nanoparticles showing various degrees of formation.

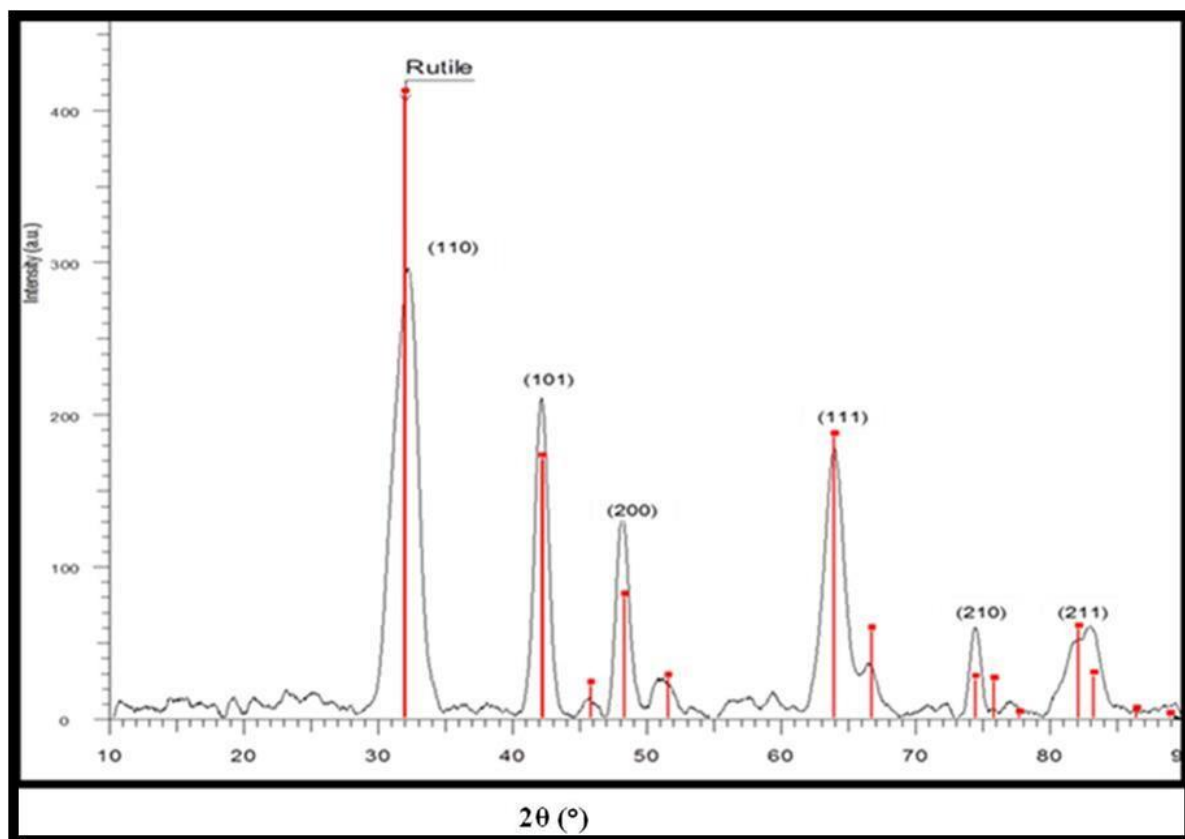


Figure 4.3 PXRD pattern of RANR confirming the exclusive presence of the rutile phase and also confirming peak anisotropy, related to the shape of the rods.

4.4.2 DPU of Au, Ni and La on RANR support

The loading of metal nanoparticles of Au, Ni and La onto RANR was done using deposition-precipitation using urea (DPU). At acidic pH, the TiO_2 surface of RANR is positively charged which prompted anionic precursor metals to electrostatically attach on the RANR support. As the hydrothermal decomposition of urea progressed, the pH increased and the surface charge density of the precursor metal anion precipitated particles was altered giving rise to particle disintegration and hence a decrease in particle size with time accompanied by a more uniform particle distribution with no distinguishable aggregation and sintering. The method was used to carry out parametric studies of wt. % of metal nanoparticles onto RANR. **Fig. 4.4** shows typical TEM images of 5 wt. % loadings of Au, Ni and La metal nanoparticles respectively onto the RANR.

At 5 wt. % metal loading, the Au, Ni and La metal catalysts were successfully deposited on RANR using DPU. **Fig. 4.4 (a)** shows some Au nanoparticles deposited at the tips of the RANR. The precipitation of Au is reported to take place very quickly and is complete within the first hour when the pH of the solution is still acidic.^{27,28} **Fig. 4.4 (b)** and **(c)** show the

distribution of the metal nanoparticles as they are deposited on the nanorods of the RANR. The metals were evenly distributed across all the tips of the RANR nanorods of the RANR.

The metal nanoparticle sizes were determined from TEM images using ImageJ. **Fig. 4.5 (a)** and **(b)** show diameter and particle size distribution of the nanorods of the RANR and the supported metal nanoparticles respectively. It was observed that at short deposition time, the average metal nanoparticle size of the deposited Au was large, but with an increase in DPU time, the size decreased coupled with a higher metal loading.²⁹ This explains the observed small particle size distribution of the metal catalyst with averages ranging from Au: 1-3 nm, Ni: 2-3 nm and La: 2-8 nm (**Fig. 4.5(b)**). The small size of the metal particles observed by TEM suggests that a strong interaction occurs between RANR support and the metal nanoparticles precipitated during deposition.³⁰

Weight % loadings of Au, Ni and La metal nanoparticles on RANR showed a similar pattern of metal nanoparticle deposition. Some metal nanoparticles were also noted to be distributed along the radial length of the TiO₂ nanorods of the RANR. **Fig. 4.6 (a)** shows a high magnification image of Au nanoparticles deposited on RANR. The phase contrast of gold nanoparticles is seen on the TiO₂ of RANR ($M_r = 79.87 \text{ g. mol}^{-1}$) because of gold's higher atomic mass ($A_r = 196.97 \text{ g. mol}^{-1}$). The atomic masses of Ni ($A_r = 58.69 \text{ g. mol}^{-1}$) and La ($A_r = 138.91 \text{ g. mol}^{-1}$) are lower than that of Au and do not show a distinct phase contrast from that of RANR. Even at higher magnification, the Ni and La metal nanoparticles are lighter in colour but contrast sufficiently from the RANR to be distinguished. **Fig. 4.6 (a)**, shows that the particle size distribution is homogenous in 8 wt. % Au/RANR. **Fig. 4.6 (b) and (c)** show the deposited Ni and La metal catalysts on the nanorods of the RANR.

Deposition of 10 wt. % loading of Au, Ni and La is shown in **Fig. 4.7**. **Fig. 4.7 (a)** shows a dense distribution of Au nanoparticles on the nanorods of the RANR. Au nanoparticles were deposited on the tips of the TiO₂ nanorods of the RANR. This is also presented in **Fig. 4.7 (b)** for 10 wt. % Ni loading. The deposition of 10 wt. % La showed uniform spatial distribution of La nanoparticles as shown in **Fig. 7 (c)**. The inserts in **Fig. 4.7** show how the Au, Ni and La are attached to the RANR to form supported catalysts.

ImageJ was used to determine average metal nanoparticle sizes. At 10 wt. % loading, the Au nanoparticles have particle sizes ranging from 2–3 nm. The Ni nanoparticles have particle size ranging from 1–6 nm while La nanoparticles are in the range 2–8 nm. **Fig. 4.7** also shows the squared tips of the RANR.

The DPU process involves vigorous stirring of RANR in the solution mixture over time ranging from 18–24 h. But the RANR did not disintegrate or get pulverised. They retained their morphology and respective dense packing of TiO₂ nanorods in their RANR structure. However, as the hydrothermal decomposition of urea progressed, the pH increased and the surface charge density of the precursor metal anion precipitated particles was altered giving rise to particle disintegration and hence a decrease in particle size with time accompanied by a more uniform particle distribution with no distinguishable aggregation and sintering. The deposition of metal catalyst nanoparticles does not expand or distort the arrangement of the nanorods in the RANR spheres.

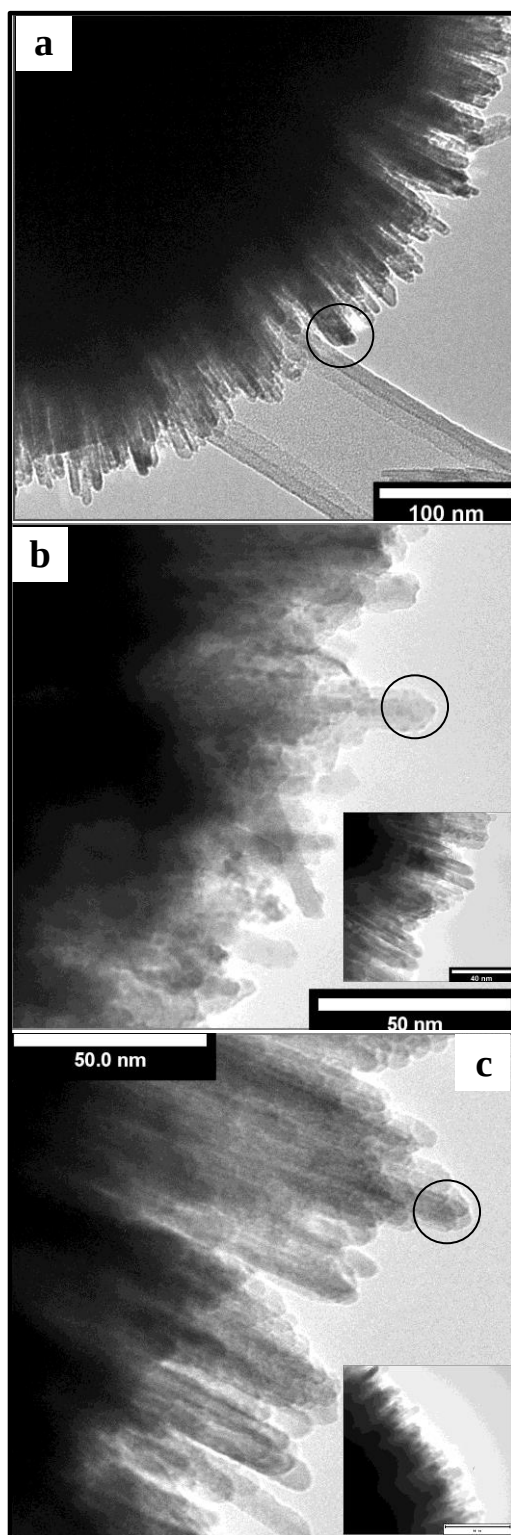


Figure 4.4 TEM image of 5 wt. % loading of (a) Au catalyst, (b) Ni catalyst and (c) La catalyst on RANR.

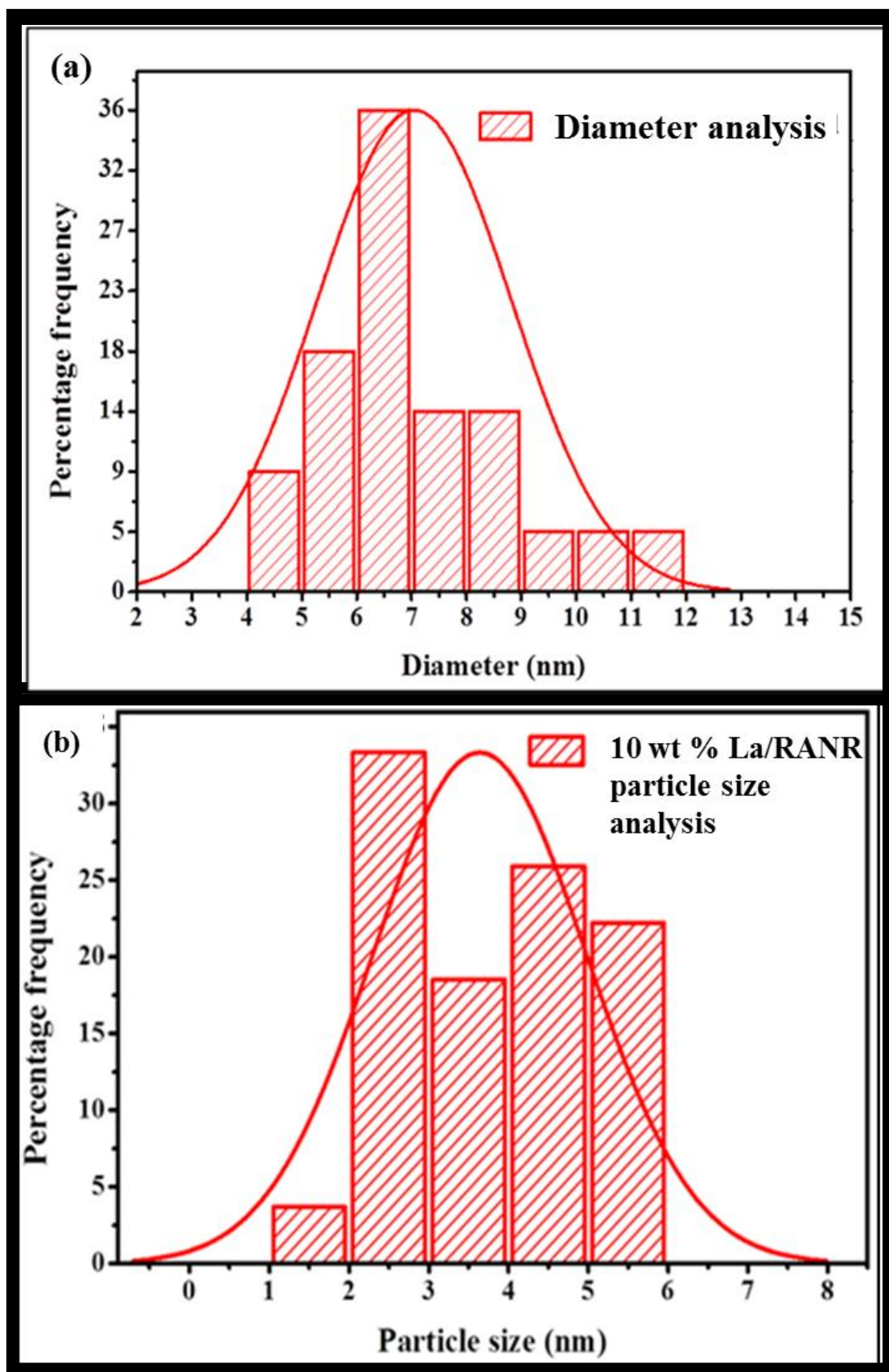


Figure 4.5 Size distribution analyses of (a) RANR nanorods (b) 10 wt. % La/RANR calcined at 500 °C and H₂ – reduced at 600 °C.

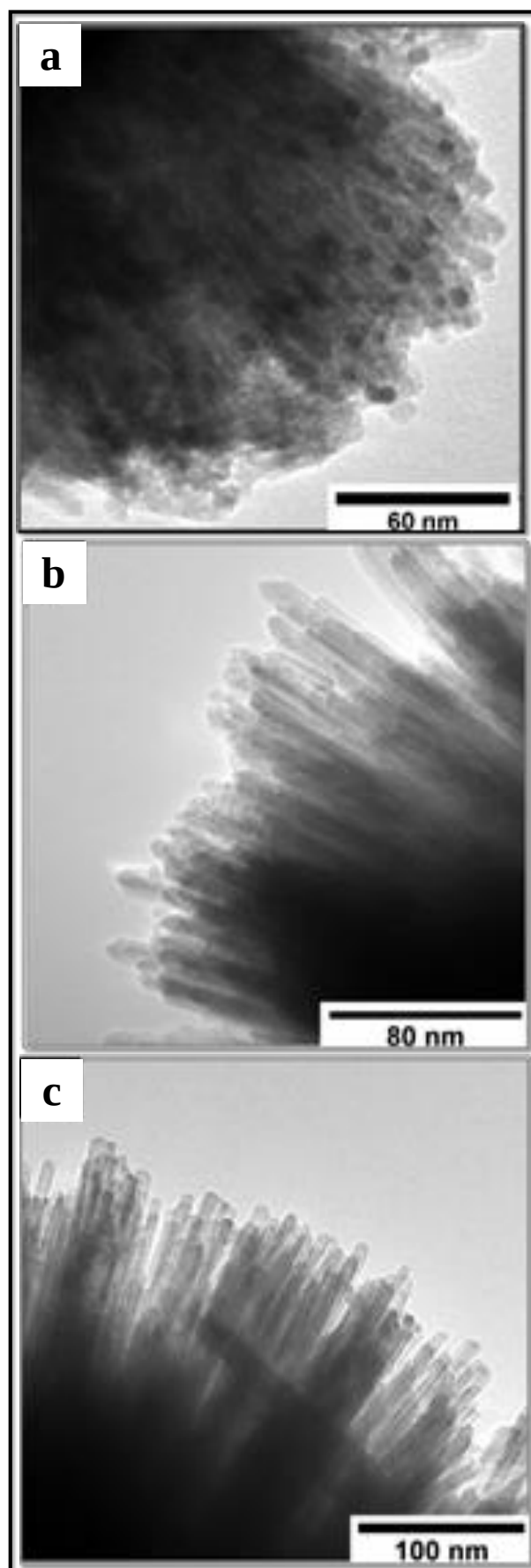


Figure 4.6 TEM image of 8 wt. % loading of (a) Au/RANR, (b) Ni/RANR and (c) La/RANR

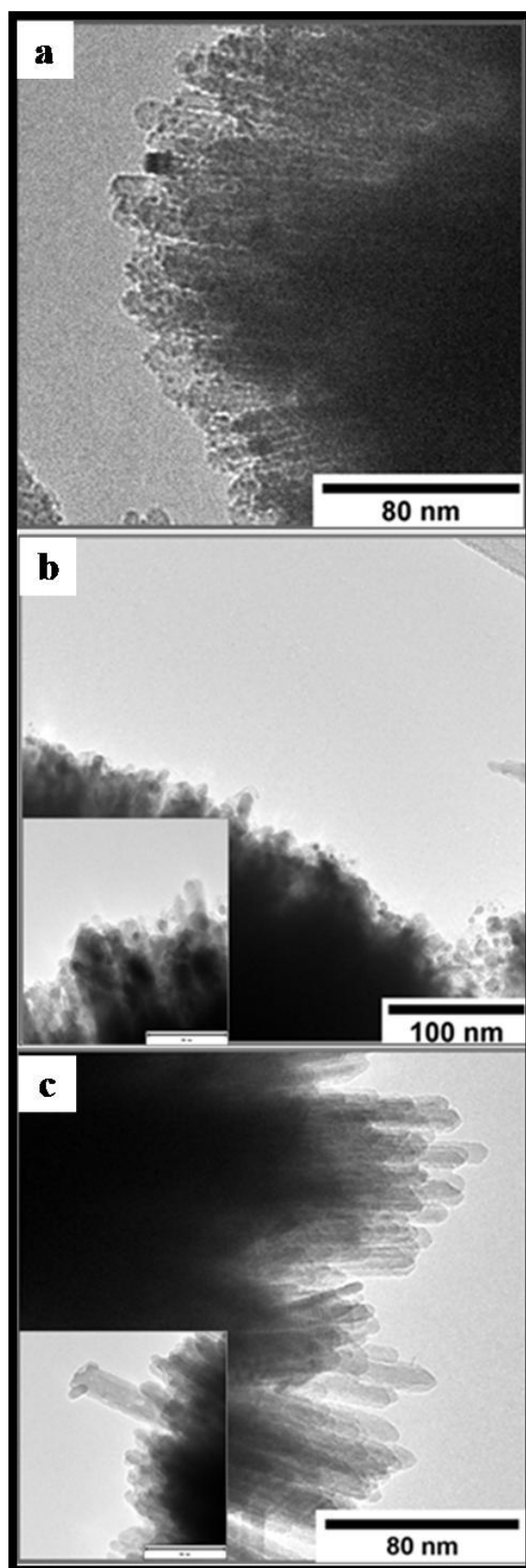


Figure 4.7 TEM image of 10 wt. % loading of (a) Au/RANR (b) Ni/RANR and (c) La/RANR.

4.4.3 PXRD analysis

Powder X-ray diffraction (PXRD) analysis of the supported catalysts showed consistent patterns for the respective different metal loadings for each metal. The peaks in each series of patterns matched the identity of respective single phases as shown in the Au/RANR PXRD patterns in **Fig. 4.8 (a)**. The major peak observed was related to the rutile phase at 2θ 32.2° (100) peak. The Au/RANR patterns in **Fig. 4.8** have characteristic small extra peaks occurring between rutile peaks 101 and 200 and also between 200 and 111 of the rutile phase due to metallic gold (ICSD collection code 44362). The peaks at 2θ values 45 and 52.1° increase in intensity with an increase in wt. % Au loading corresponding to an increase in diffracting material. PXRD peaks of Ni/RANR shown in **Fig. 4.8 (b)** also had similar patterns that matched with those of pure rutile. However, additional peaks were observed at 2θ values 29.3, 39.1 and 47.2° (ICSD collection code 53807). These peaks were attributed to Ni metal. The peaks increased in both intensity and increase in metal wt. % loading.

The PXRD pattern in **Fig. 4.8 (c)** showed patterns of the La/RANR catalysts. The patterns exhibited a series of peaks that occurred in the PXRD of the pure rutile phase. However there was no distinguishable peaks that may be attributable to a La phase. This could be due to La particles being too small. However, La peaks were expected to appear at 2θ values of 12.1° and 22.3° (ICSD collection codes 1950 and 104656). Particle size analysis in **Section 4.4.2** showed La particles having a size range 2-8 nm. This size range was in the correct range to give a peak in a PXRD pattern. Detailed TEM analysis showed that La particles deposited around the tips of the rutile nanorods of the RANR.

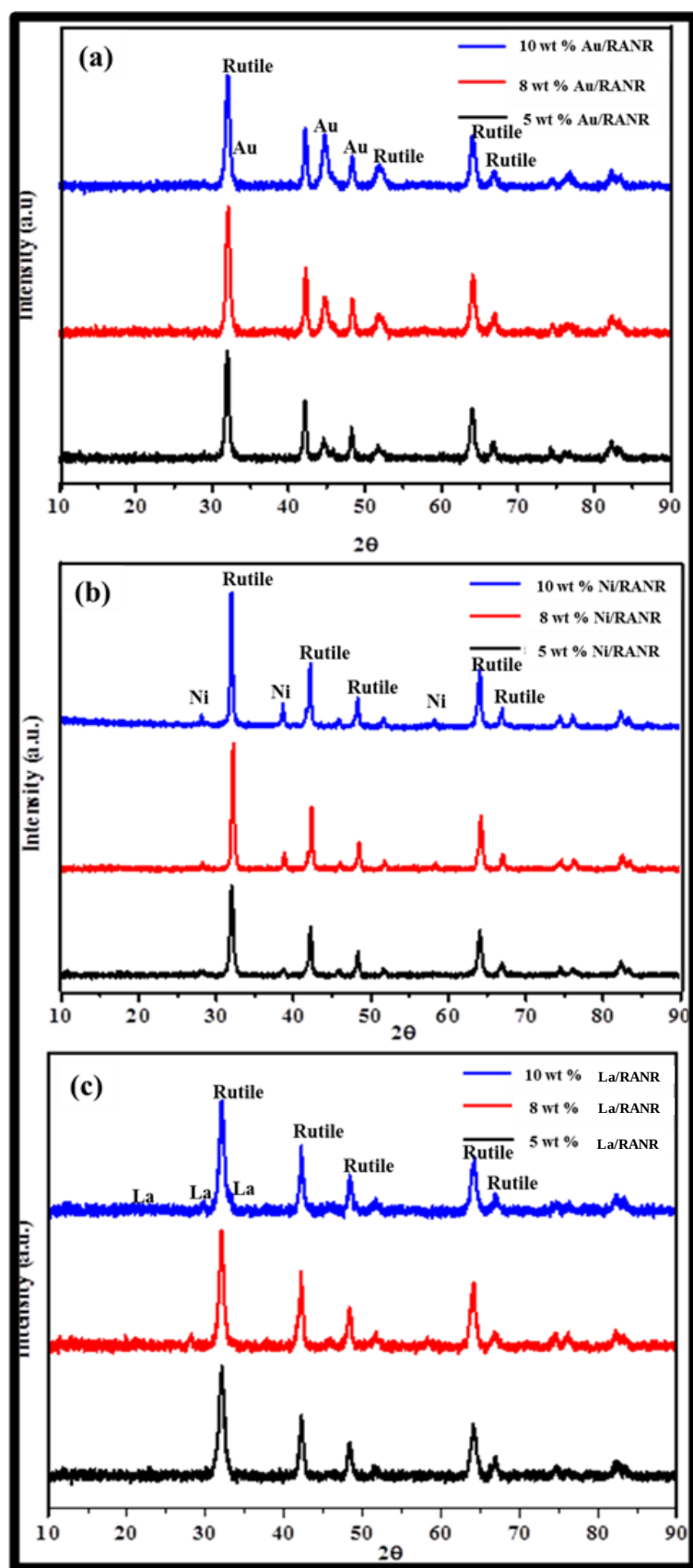


Figure 4.8 PXRD pattern of supported Au/RANR (a), Ni/RANR (b) and La/RANR (c) calcined at 700 °C for 4 hr.

4.4.4 EDS analysis of the supported catalysts

Energy dispersive X-Ray spectroscopy (EDS) analysis was carried out only on the 10 wt. % loaded RANR to confirm the elemental composition of the materials. **Fig. 4.9** shows EDS spectra of the 10 wt. % supported catalysts. **Fig. 4.9 (a)** showed peaks confirming the presence of Au. A peak due to Ti was due to the rutile TiO_2 nanorods of the RANR. The Cu peak was due to the copper grid used to load the catalyst sample for EDS analysis. **Fig. 4.9 (b)** showed peaks confirming the presence of La in the 10 wt. % La/RANR catalyst. The La metal dispersed energy at a wavelength that is similar to that of Ti. Therefore the La peaks overlapped those of Ti hence the metals are identified on the same peaks. However, Ti has electrons in the $K\alpha_{1,2}$ shells and gives EDS count at 4.5 KeV. La does not have electrons in the K shell but in the $M\alpha$ that are excited and give EDS count at 0.833 KeV. **Fig. 4.9 (c)** showed peaks corresponding to Ni. The Ni peak overlap with that of Cu at 1 and 7.5 KeV. **Fig. 4.9 (c)** also shows a small Si peak which can be attributed to particles of glass from the glassware used in the preparation of the materials or more likely to some silica contaminant in the film.

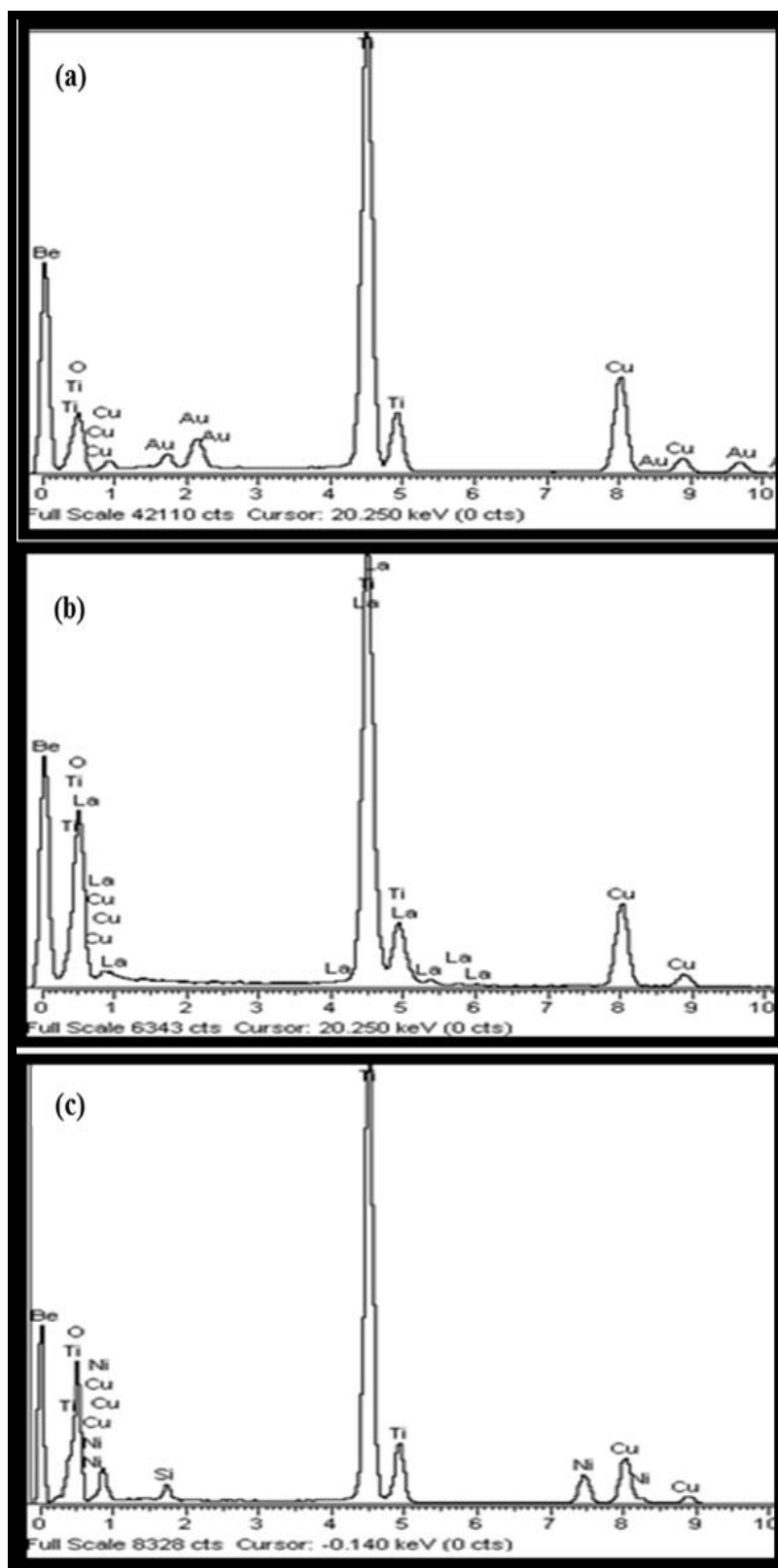


Figure 4.9 EDS spectra of supported metal nanoparticles on RANR (a) 10 wt. % Au/TiO₂ (b) 10 wt. % La/TiO₂ and (c) 10 wt. % Ni/TiO₂.

4.4.5 BET surface area measurements

Surface area studies using BET showed how the deposition affected the surface area and porosity of the RANR. The surface area and pore volumes of the supported catalysts obtained from DPU decreased with an increase in metal loading. The unloaded RANR support has a surface area of $50 \text{ m}^2 \text{ g}^{-1}$. The BET surface area of the unloaded RANR is due to the supported catalyst metal nanoparticles. This is because the loaded nanoparticles had a high density coverage on the RANR nanorods support.³¹ The supported catalyst metal nanoparticles covered the pores on the support surface. **Table 4.1** showed both surface area and pore volumes decreasing relative to that of unloaded RANR. M. This may be compared to the observations made by Khoudiakov *et al.* who reported that Au supported on Fe_2O_3 was observed to undergo six-to-seven fold decrease in surface area on heat treatment of the catalyst samples.¹⁸ This is despite the fact that Fe_2O_3 is a different material with a different morphology to RANR. The previous reports presented values ranging from $80\text{-}100 \text{ m}^2 \text{ g}^{-1}$ which decreased slightly after metal loading.^{19,32} This is in agreement with what was observed in this work. The corresponding surface areas and pore volumes of the three samples after drying at 80°C and again after calcination at 700°C for 4 h are presented in **Table 4.1**. The surface areas of all three Au/ TiO_2 samples decreased to between 33 and $50 \text{ m}^2 \text{ g}^{-1}$ while that of Ni/ TiO_2 samples decreased slightly within a 43 to $49 \text{ m}^2 \text{ g}^{-1}$ range and the La/ TiO_2 ranged from 36 to $44 \text{ m}^2 \text{ g}^{-1}$.

The observed decrease in surface area trend of the overall supported catalyst complement PXRD and TEM analyses, that showed increase in particles size distribution with an increase in metal loading. More pores on the RANR support material were blocked with increase in loading coupled with increase in spatial distribution and particle size.

Table 4.1 BET surface areas and pore volumes of Au, Ni and La nanoparticles on RANR support calcined at 700 °C for 4 h.

Sample:	Surface Area m ² g ⁻¹	Pore Volume cm ³ g ⁻¹
Plain RANR	50	0.22
5 wt. % Au/RANR	50	0.22
8 wt. % Au/RANR	42	0.20
10 wt. % Au/RANR	33	0.15
5 wt. % Ni/RANR	49	0.20
8 wt. % Ni/RANR	46	0.20
10 wt. % Ni/RANR	43	0.20
5 wt. % La/RANR	44	0.16
8 wt. % La/RANR	37	0.13
10 wt. % La/RANR	36	0.11

4.4.6 TPR analysis of supported catalysts

TPR profiles of the metal nanoparticles supported on the RANR are shown in Fig. 4.10. At acidic pH, the TiO₂ surface of RANR is positively charged which prompted anionic precursor metals to electrostatically attach on the RANR support. The profiles in Fig. 4.10 (a) are for the supported Au/RANR. The Au/RANR materials have profiles characterised by a reduction peak around 100 °C. Previous studies reported a similar low-temperature reduction peak like this for Au/TiO₂ samples.^{33–35} The observed peak in Fig. 4.10 (a) is attributed to the reduction of the Au nanoparticles. This confirms that the DPU loaded Au was in the oxidised state as also reported in former work²⁹ and support previously reported results that the Au/TiO₂ precursor decomposes in air due to the instability of Au₂O₃ to form Au⁰.³⁶ This observed phenomenon is attributed to the extent of interaction between the support and the deposited metal catalyst which vary from one support to another for the same catalyst.³⁷ The interactions are influenced by surface energetics and morphology of the support material. The

peak intensities in **Fig. 4.10 (a)** show a steady increase with increase in wt. % gold loading on the RANR support.

Reduction profiles of supported Ni catalysts in **Fig. 4.10 (b)** show that peak intensities increased with an increase in wt. % loading, with the 10 wt. % having the widest and most intense peak. However, the peak intensity of 5 wt. % Ni/RANR is greater and narrower than that of 8 wt. % Ni/RANR. This could be due to the Ni particles of the 5 wt. % Ni/RANR having a smaller particle size thus reducing more rapidly than the large particles of the Ni particles of 8 wt. % Ni/RANR. The wide regions of H₂ consumption extend from 300 to 610 °C with a half-width maximum at 500 °C. Previous studies reported that Ni²⁺ is fully reduced at 330 °C to Ni⁰.³¹ However, this value varies with the support on which the Ni is supported. Similar to supported gold catalysts, the Ni metal interacted with different support materials to different extents thus influencing the reducibility of the metal. G. Yuan *et al.*³¹ reported that the Ni/RANR forms a peak at 520 K with a subsequent wide region of H₂ consumption extending into the final isothermal temperature at 603 K with an ultimate return to baseline. This observation is a shift from the observed reduction range including difference in the positions of the peaks and their relative intensities for supported Ni catalysts and other zeolite supports such as TiO₂, Fe₂O₃ and SiO₂.

Fig. 4.10 (c) presents TPR profiles of La/RANR catalysts. The profiles are characterised by wide peaks with regions spanning from 400 to 900 °C. The profile of the 5 wt. % La/RANR is characterised by two peaks at $\approx$ 600 and 850 °C. This phenomenon is elucidated by

Su Khine *et al.* who postulated that the distinctive reduction peaks at different temperatures could signify that there exist various types of O²⁻ species at different mobility that participate in the reaction with H₂.³⁸ Previous studies revealed different reduction temperatures due to the nature of the support on which the La was loaded.³⁹ In this study, we report a reduction temperature of $\approx$ 600 °C for La₂O₃ supported on RANR as presented in **Fig. 4.10 (c)**. The shift to higher reduction temperature as compared to previous studies highlighted above could be attributed to the greater extent of interaction between the La and the RANR support.

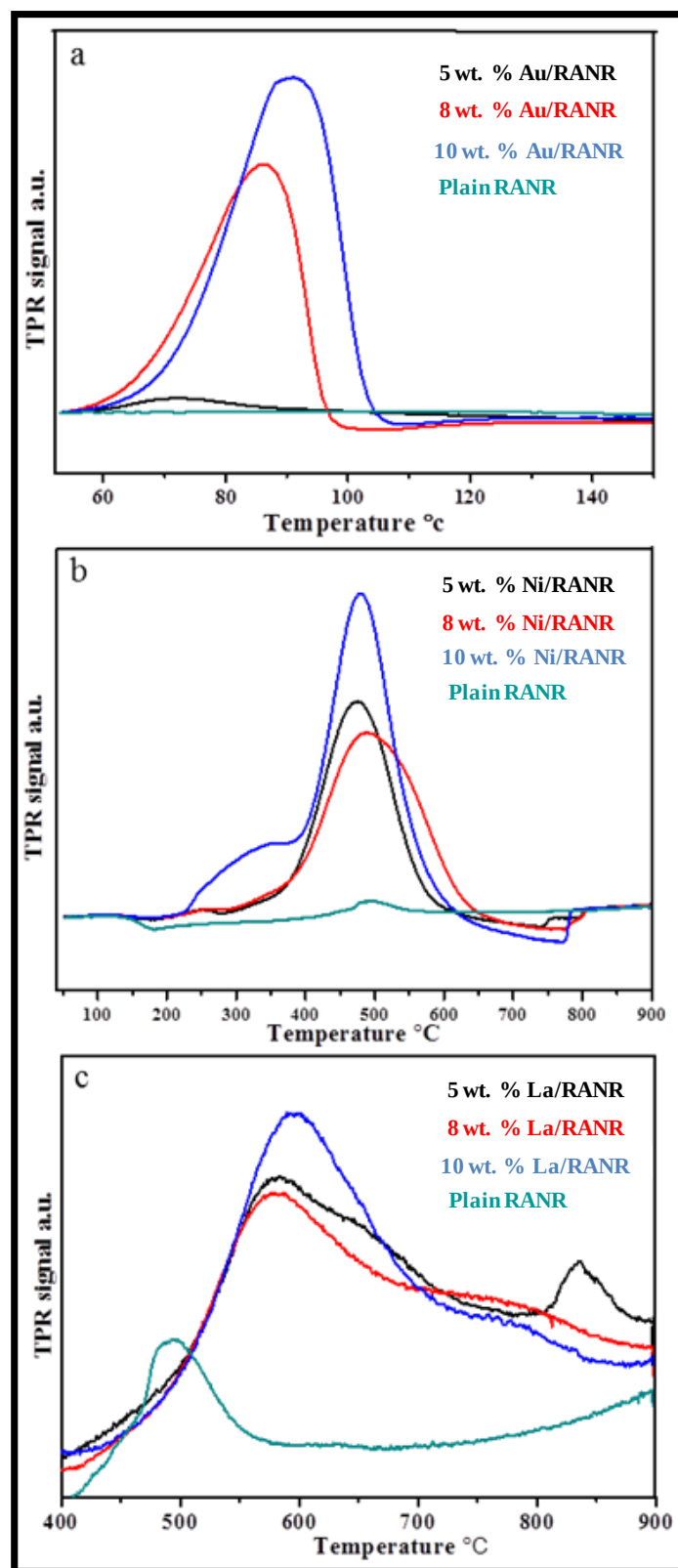


Figure 4.10 TPR spectra of supported (a) Au/RANR (b), Ni/RANR (c) and La/RANR, calcined at 700 °C.

The rutile peak is more intense at a reduction temperature of 500 °C in **Fig 4(c)** than it is in **Figs 4 (a) and (b)**. This is mainly because of the reduction temperature of rutile TiO_2 that is at a lower temperature than the reduction temperature of La metal occurring around 600 °C. The shift of the La reduction peak to higher temperatures enabled the rutile peak to intensely exhibit itself than in **Fig 4(b)** where it is suppressed with Ni peaks occurring around the same reduction temperature as that of rutile. Comparison of the TPR response of profiles in **Fig. 4.10 (a) and (b)** for Au and Ni respectively, shows that the deposition of La on RANR influences TPR behaviour rendering the La^{3+} less susceptible to reduction hence higher reduction temperatures are observed. These reduction temperatures are critical in determining suitable reaction thermal conditions in catalysis. In this work, reduction was done in a CVD setup prior to synthesis of shaped carbon nanomaterials so that the metal oxides (Au_2O_3 , NiO and La_2O_3) loaded on the RANR support are reduced to metallic supported catalysts (Au/RANR, Ni/RANR and La/RANR) that have desirable catalytic properties and characteristics. The catalysts were used for the synthesis of shaped carbon nanomaterials.

4.5 Conclusions

The hydrothermal method of synthesis was used to successfully synthesise RANR powders using TiCl_4 as the starting material. The RANR spheres have an average diameter of 1-2.5 μm and comprised nanorods packed radially (i.e. with a common crystallographic axis for all rods), with a diameter range of 2-13 nm and lengths ranging from 500–650 nm. The “as prepared” RANR powders provide a good support for preparing supported catalysts. Hydrothermal decomposition of urea was successfully used to load Au, Ni and La nanoparticles on the RANR support.

Detailed studies were done for the preparation method in particle size, effect of wt. % loading, surface area analysis and reducibility at different metal loading. At acidic pH, the TiO_2 surface of RANR is positively charged which prompted anionic precursor metals to electrostatically attach on the RANR support. As the hydrothermal decomposition of urea progressed, the pH increased and the surface charge density of the precursor metal anion precipitated particles was altered giving rise to particle disintegration and hence a decrease in particle size with time and a more uniform particle distribution with no distinguishable aggregation and sintering. The supported Au nanoparticles had particle sizes ranging from 1–3 nm while the supported Ni nanoparticles had particle sizes ranging from 2–3 nm and the supported La nanoparticles were in the range 2–8 nm. The catalysts in the “as prepared” state

are in the oxidised forms Au_2O_3 , NiO and La_2O_3 but were reduced to metallic states by calcination and subsequent reduction in hydrogen.

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Chapter 5

Synthesis of carbon nanofibers over supported lanthanum nanoparticle metal catalysts on RANR: A parametric study

5.1 Introduction

The use of materials on the nanoscale is receiving extensive attention, in attempts to design and synthesize new functional materials with novel properties. This has also opened avenues for new materials that previously were not well known or less researched. Lanthanum (La) has recently been synthesized to catalyse the synthesis of carbon nanomaterials for different applications.¹ Carbon nanotubes (CNTs), carbon nanofibers (CNFs), single and multi-walled carbon nanotubes (SWCNTs/MWCNTs) are of interest due to their desirable properties such as electrical behaviour and mechanical strength. In the chapter presented here, a parametric study of the synthesis of CNFs via the CVD of acetylene under hydrogen (C_2H_2/H_2) over La nanoparticles supported on RANR (La/ RANR) was conducted. Here the mechanism of growth (i.e. base or tip) was monitored by varying parameters such as gas: flow rate, temperature, CVD reaction time and % weight La loading. These parameters were varied during the syntheses to determine how the supported catalyst performed in terms of its activity and selectivity as well, and to determine the nature of the carbon nanomaterials that were prepared. Characterisation of the catalysts and the CVD products was performed by TEM, SEM, PXRD, LRS and TGA.

5.2 Literature review

Shaped carbon nanomaterials (SCNMs) are structures of any shape, made of carbon atoms and having diameter on the nanometer scale.² SCNMs may take shapes such as: spheres, sheets, fibers, rods, sticks, horns, flakes or simply amorphous carbon material.² In recent years CNFs and mostly CNTs have attracted much attention among researchers throughout the world due to their peculiar microstructural morphology, unique properties and potential applications in various fields.³ CNFs are characterised by being many times stronger than steel, harder than diamond, having an electrical conductivity higher than that of copper and thermal conductivity higher than that of diamond^{4,5}. CNFs also show promise for a wide range of potential applications such as: field emission displays, fuel cells, electronic devices, catalysts and biosensors⁶⁻⁸. Numerous previous studies have reported on the synthesis of different shapes of carbon nanomaterials over a wide range of supported and unsupported catalysts using different carbon sources. Reports have included the catalytic preparation of simple and coiled CNFs from coal gas and acetylene by the catalytic chemical vapour deposition (CCVD) method with catalysts such as: ferrocene, supported gold and Co supported on silica respectively^{3,6,9-12}.

Previous studies have reported on the hydrothermal growth of titania with tuneable phases, shapes and 3D dandelion-like structures^{13,14}. Here the overall 3D dandelion-like structures were spherical with average diameters of about 1.5 – 2 μm and were composed of many loosely radially packed nanometer-scale crystals with square-shaped ends.¹⁵ These 3D artificial hierarchical dandelion-like structures have the advantage of preserving the novel nanometer-scale properties, while providing the convenience of storing and handling metal nanoparticles that could be spatially dispersed along the radial lengths of the nanorods.¹⁴

Lanthanum, like other heavy metals, has been found in industrial and other chemical waste products.¹⁶ Unfortunately, its recovery from these waste products has been minimal due to its limited uses.¹⁷ Nonetheless, it has been used in a few instances in catalysis. For example, lanthanum has been used as a co-catalyst/co-dopant in the preparation of a TiO_2 supported catalyst that was made by a homogeneous hydrothermal precipitation method.¹ Similarly, a La–N co-doped TiO_2 catalyst has shown superior photocatalytic activity to plain TiO_2 for the decomposition of Rhodamine B under visible-light irradiation.¹⁸ Likewise La has been used as a co-catalyst in a mixed metal oxide catalyst (i.e. SrTiO_3), where the resultant material was

able to photodegrade methylene blue.¹⁹ On the other hand, La has also been used to co-dope TiO₂ nanocrystals with carbon, where the enhanced photocatalytic activity of this and other such La-doped TiO₂ nanocrystals has been attributed to the modification of the optical properties as well as surface states of TiO₂.^{1,20}

However, based on extensive literature search, it appeared that supported La had never been used unaided as a catalyst in the synthesis of SCNMs. Consequently it was hypothesised that due to the spherical morphologies and radial loose packing of the rutile titania nanorods into RANR structures, these would have been able to provide unique support structures for La nanoparticles, resulting in novel La/RANR catalysts for this purpose. Hence in this chapter, La/RANR catalyst was synthesized, characterized and then tested for their ability to catalyze the formation of SCNMs from acetylene by the CVD method. Here it was hoped that if La was a successful catalyst, it could in the future be recovered from environmental wastes to be used for this and various other applications.

5.3 Experimental

5.3.1 Preparation of La supported catalysts

La catalysts supported on RANR were synthesized in this work using the hydrothermal method that was introduced in **Section 3.1.3** and explained in detail in **Chapter 4**. In brief, both LaCl₃ (solid) and TiCl₄ (liquid) were obtained from Sigma Aldrich. A hydrothermal method was used to prepare the RANR at 200 °C. Deposition-precipitation using urea (DPU) was used to deposit La onto the RANR according to calculated loadings i.e. 0.5, 1, 2, 5, 8 and 10 wt. %. The DPU experiments were carried out at 80 °C for 24 h.

5.3.2 Synthesis of CNFs

CNFs were prepared in a horizontal quartz tube reactor as shown in **Fig. 3.1** (see **Section 3.14**), in which the La/RANR catalyst was placed in a quartz boat positioned at the centre of the furnace. The temperature maintained at the centre of the furnace was varied to 300, 400, 500, 600 and 700 °C. Acetylene gas was introduced into the tube reactor at a flow rate that was varied to: 50, 75 and 100 cm³ min⁻¹ with hydrogen (being used as the carrier gas) set at the same flow rate. For all reactions, the furnace's temperature was ramped at a heating rate of 10 °C min⁻¹ to the pre-set reaction temperature and then held at that temperature for a pre-set period of time. Acetylene and H₂ (the carrier gas) were both introduced at a uniform pre-

set flow rate. After each reaction was completed the furnace was allowed to cool down to room temperature under the hydrogen gas which was allowed to flow throughout the duration of the reaction.

5.3.3 Characterisation of catalysts and carbon products

The crystallographic phases of the La/RANR catalysts were determined by obtaining PXRD patterns using the Bruker D2 Phaser diffractometer in a 2θ range from 7 to 120° using Co $K\alpha$ radiation wavelength (λ) of 1.79 nm. The as-synthesized CVD products were collected and analysed by: TEM, SEM, and LRS. For TEM analysis, the samples were prepared by dispersing a small amount of the material in methanol under sonication. The drops of the dispersed material were placed on an holey carbon Cu micro-grid. A FEI TEM Spirit operated at a voltage of 120 kV was then used. For SEM analysis, the material removed from the tube reactor was directly mounted on carbon tape on a sample holder stub. A FEI SEISS FIB was used for SEM analyses. The average particle size was determined using ImageJ and statistical analysis was done using particle size measurements from TEM and SEM micrographs. A minimum of 200 particles were counted from these micrographs and using a normal Gaussian curve, the particle sizes were established statistically. EDS analyses of the chemical compositions of the carbon nanomaterials and catalyst surfaces were performed using the TEM FEI Spirit 120 kV EDS.

5.4 Results and discussion

5.4.1 PXRD analysis

The PXRD patterns of the unloaded RANR, supported La/RANR and La/RANR-SCNMs are shown in **Figs. 5.1 (a)-(c)**. The PXRD pattern in **Fig. 5.1(a)** showed that unloaded RANR was composed of nanorods that were arranged in the standard tetragonal rutile structure with orientation in the (110) plane.²¹ The PXRD pattern of the supported La/RANR catalyst predominantly exhibited peaks of pure rutile (which occurred at a 2θ value of 32.5° for the major rutile peak, and minor peaks at 42.5 , 48.0 , 52.1 , 64.0 , 66.5 , 75.0 and 82.2° respectively). La showed peaks occurring at 2θ values of 30.1° and 15.3° respectively as shown in **Fig. 5.1(b)** and **Appendix A**.

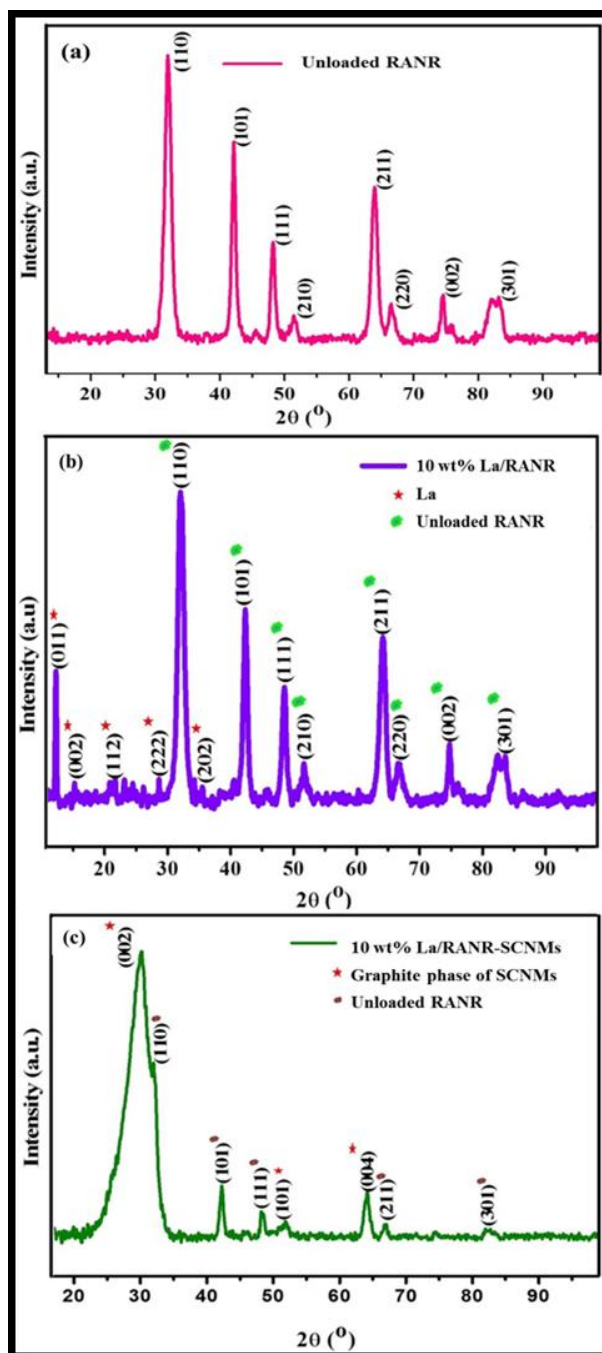


Figure 5.1 PXRD patterns of: (a) RANR hydrothermally prepared at 200 °C for 24 h, (b) 10 wt. % La/RANR prepared using DPU at 80 °C for 24 h, (c) SCNMs from CVD at 700 °C, 2 h and 75 mL min⁻¹ on supported catalyst (SCNMs on 10 wt. % La/RANR).

Both PXRD patterns in **Fig. 5.1(b)** and **(c)** showed very similar, but minor peaks that were due to La at 2θ values of 26.5° and 28.0°. ²² In this study, the La peak corresponded to that identified on the pattern for the La catalysts in previous studies. ²³ This implied that La is not crystallographically fused into the TiO₂ matrix of the La/RANR catalyst. The PXRD pattern in **Fig. 5.1(c)** showed a broad peak that is at 2θ value of 28.1°. This peak has been identified

as being predominantly due to graphitic carbon nanostructures²⁴, synthesized over the 10 wt. % La/RANR catalyst. Here, it was observed that the carbon peak overlapped with the rutile and La peaks. PXRD analysis of the La/RANR catalyst showed new peaks appearing at 2θ values of 12.3° and 22.1° for higher wt. % loadings of La (see **Appendix A**). In previous studies by M. Salavati-Niasri *et al.*, it was observed that calcining La_2O_3 at 600°C for 2 h transformed it into a high purity phase with a hexagonal structure.²² This correspond to high calcination temperatures at 700°C , for 2 h that resulted in the transformation of a pure phase of crystalline La that appeared at the 2θ values of 12.3° and 22.1° . It can be concluded that the combined effect of calcination and reduction facilitated the transformation of the La metal to a phase which appeared at lower angles on the PXRD scale of the La/RANR catalyst. In addition to the rutile peaks, the PXRD peak patterns of the supported La/RANR catalysts shown in **Fig. 5.1(b)** had peaks which occurred at 2θ values of 21.3° , 25.4° , 29.2° and 36.3° which were attributed to minor peaks of the temperature enhanced La-metal transformed phase.

5.4.2 Transmission and scanning electron microscopy

Figs. 5.2 (a)-(b) show a SEM and a TEM micrograph of La metal catalyst nanoparticles supported on spherically shaped RANR. The SEM micrograph in **Fig. 5.2(a)** showed the 3D morphology of the RANR on which the La nanoparticles were dispersed. The TEM micrograph showed supported La catalyst nanoparticles (see encircled regions in **Fig. 5.2(b)**) spatially distributed along the radial length of the rutile nanorods (see arrow in **Fig. 5.2(b)**) prior to use in these CVD reactions. The nanorods within the RANR had average diameters of 15 nm and lengths which ranged from 500 to 650 nm. The La nanoparticles had diameters which ranged from 2 – 8 nm as measured using the ImageJ particle size analyser.

Previous studies have reported on the nucleation and growth of CNFs by exposure of a transition metal surface to a hydrocarbon gas under low pressure.²⁵ In a similar way, La nanoparticles supported on RANR were exposed to C_2H_2 diluted with H_2 at flow rates which varied (i.e. 50, 75 and 100 ml min^{-1}) in a CVD process that was carried out at temperatures that ranged from $300 - 700^\circ\text{C}$. Here it was observed that the morphology of the catalyst nanoparticles played a critical role in the control of the morphology of the CNFs. Previous studies on the CVD synthesis of CNFs over Ni showed that individual nanoparticles may have independently affected these fibers during the reaction, having given rise to variations in their thickness.²⁶ However, in this work we observed that individual La of the La/RANR

catalyst particles does not individually affect the properties of the CNFs synthesised. This is attributable to the La particles sintering during the reaction to form larger sized particles (51 nm) as shown in **Fig. 5.3**. The sintering was facilitated by the dislodging of the La particles from the RANR support during CNFs tip growth. Neighbouring La metal particles came together forming large sized particles ranging 20–600 nm. This is evidenced by the large diameter sized particles observed after the synthesis of CNFs (**Fig. 5.4**). Y. Li *et al.* have also observed that the structure of SCNMs formed in a catalysed reaction is closely related to the properties of the metal particles, the reaction conditions and the pre-treatment of the catalyst.²⁷ Here it was observed that the mean particle size of the La changed during CVD under the different sets of reaction conditions. This was because the La particles sintered and agglomerated as the reaction proceeded. This resulted in CNFs of thicker diameters than what was suggested by the initial La particle sizes. **Fig. 5.2** (c) is a size analysis of the La nanoparticles showing that they had a size range of 2–9 nm with a mean particle size of about 6 nm.

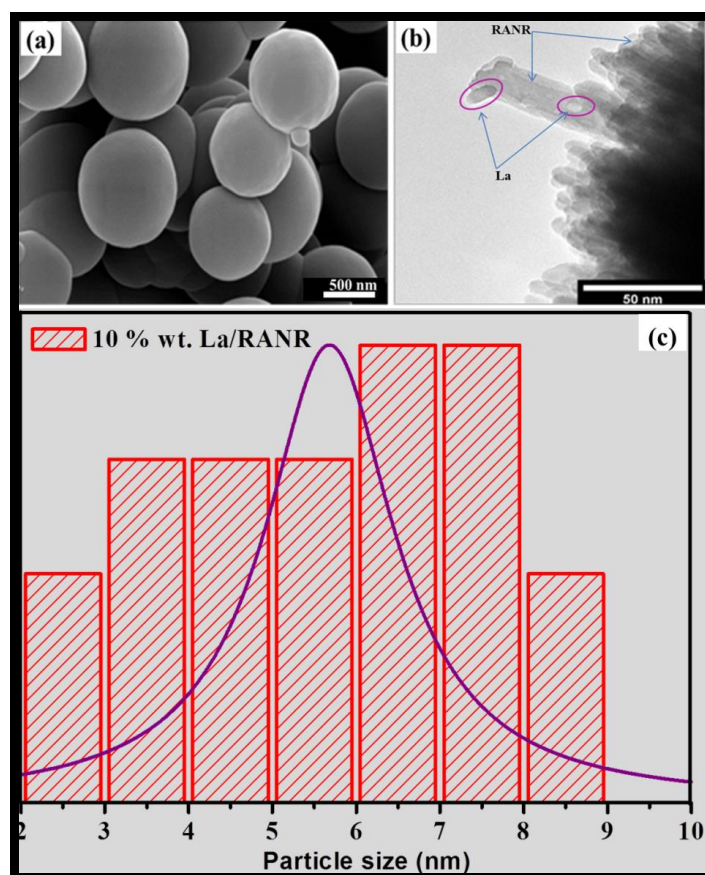


Figure 5.2 (a) SEM micrograph of spherical 10 wt. % La/RANR nanoparticles that were used in the CVD synthesis of CNFs at 700 °C. (b) TEM micrograph of the 10 wt. % La/RANR. (c) Particle size analysis of La nanoparticles.

Similar studies by M. Kawaguchi *et al.* in the growth mechanism of regularly coiled CNFs, through acetylene/hydrogen pyrolysis on unsupported Ni powder at 300–1000 °C, have shown that they grew exclusively from the tips of the Ni catalyst particles.²⁸ This may explain the growth of CNFs over the La/RANR catalysts as La was observed on many of the tips of the CNFs (see insert in **Fig. 5.3(a) and (b)**). This suggested, at least in some instances, that tip-growth had occurred.²⁹ In other cases CNFs were observed to have grown bi-directionally from one catalyst particle (see arrow in **Fig. 5.3(c)**) with homogeneous thickness and characteristic length. The La particles were not observed at the tips of the CNFs (**Fig 5.3 (d)**).

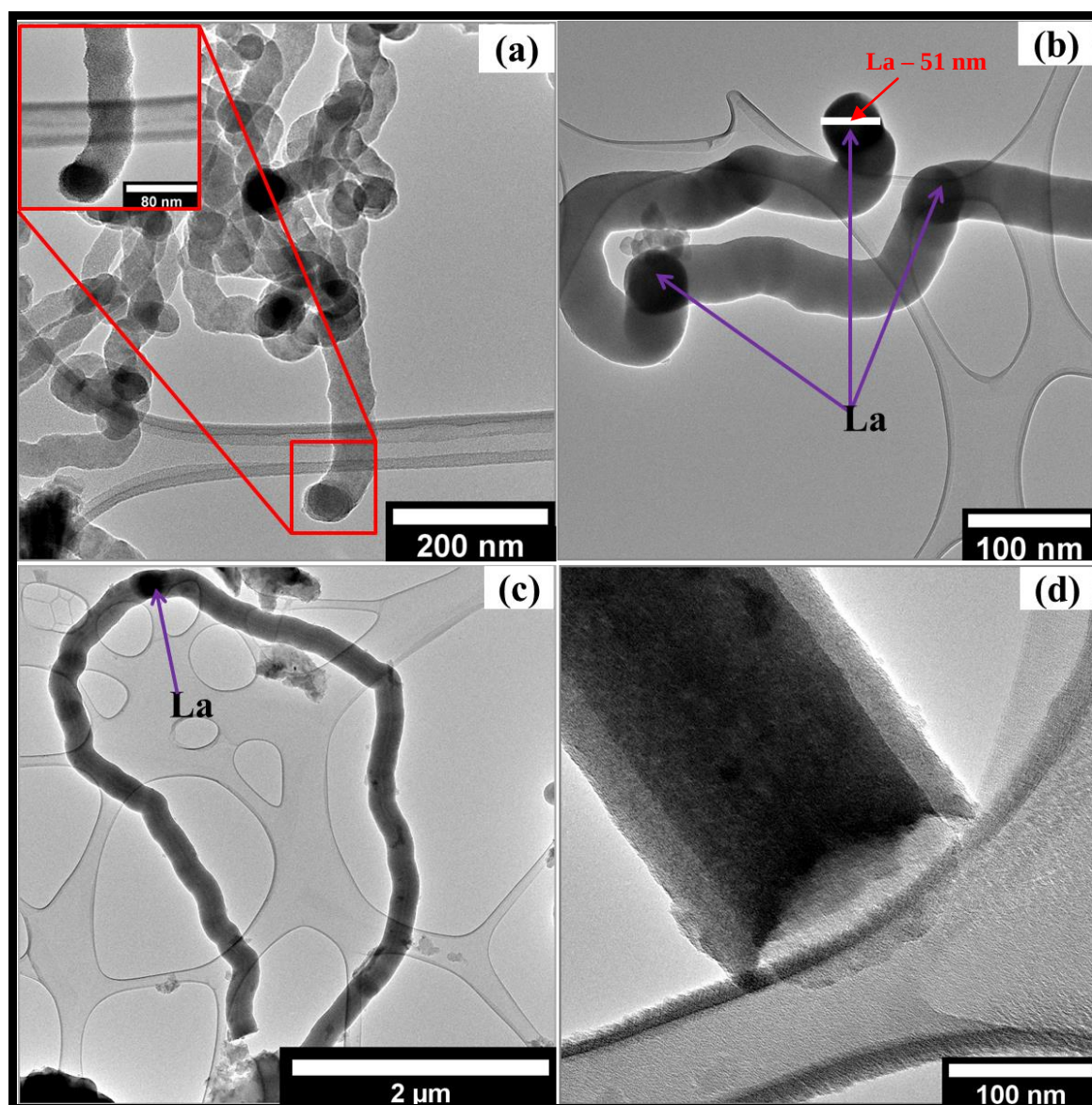


Figure 5.3 TEM micrographs of CVD-synthesized CNFs at: (a) 5 wt. % La/RANR (b) 8 wt. % La/RANR and (c and d) 10 wt. % La/RANR at 700 °C for 2 h and a flow rate of 100 mL min⁻¹.

The inserted TEM micrograph in **Fig. 5.3(a)** is a higher magnification showing how La nanoparticles had been displaced from the RANR nanorods and had given rise to long CNFs. In particular, the inserted TEM micrograph in **Fig. 5.3(a)** revealed that the size of the La nanoparticle (c.a. 40 nm) determined the thickness of the CNF (c.a. 40 nm) i.e. the diameter of the fiber was roughly equal to the diameter of the La nanoparticle around which it grew. Equally, it appeared that the La nanoparticles enabled carbon atoms to deposit, dissolve and then condense into networks that grew into CNFs i.e. La nanoparticles catalysed their growth. It was also noted that at higher wt. % of La loadings more graphitic CNFs were synthesized (see **Section 5.4.3**).

The average diameter of the CNFs synthesized by the La/RANR catalysts at 5 wt. % loadings was 40 nm while the lengths ranged from 200 nm – 100 μ m. However, La nanoparticles still attached to the RANR had an average particle size of 3 – 6 nm (see particle size analysis in **Section 4.4.2**). This implied that upon being dislodged from the support, the La nanoparticles sintered to form large particles that seeded the growth of CNFs with thicker diameters. This trend of the La nanoparticles being dislodged from the support was observed throughout the whole range of wt. % loadings (i.e. 5 – 10 wt. %) as well as all temperature and flow-rate variations. However, it was observed that changing the reaction parameters for the CVD synthesis brought about significant changes to the nature of the CNFs produced. For instance, the 5 wt. % La/RANR catalysts exhibited exceptional catalytic performance (**Fig. 5.7**) across the whole parametric range, while lower loadings resulted in the synthesis of amorphous carbon (see **Fig. 5.6**). On the other hand, the 8 wt. % La/RANR catalysts exhibited moderate catalytic performance across the whole parametric range (**Figs. 5.5 (a)-(d)**).

Fig. 5.4 presents the fiber thickness analysis of the CNFs that were synthesised over the 5 – 10 wt. % La/RANR catalysts at 700 $^{\circ}$ C for 2 h and a flow rate of 100 mL min⁻¹. The average diameter of the CNFs ranged from 40 – 270 nm while that of the supported La catalyst was shown to have average diameter of 6 nm. This size difference further confirmed that sintering had taken place during CNFs synthesis (348 nm) as shown in **Fig. 5.5**. The sintering was facilitated by the dislodging of the La particles from the RANR support during CNFs tip growth. Neighbouring La metal particles came together forming large sized particles ranging 20 – 600 nm. This is evidenced by the high diameter sized particles observed after the synthesis of CNFs (**Fig. 5.4**). Detailed analysis revealed that the average fiber thickness increased with increased wt. % metal loading as shown in **Fig. 5.4** The 5 wt. % loading had CNFs of average diameter of 40 nm while 8 and 10 wt. % loadings had 250

and 270 nm respectively. It could be concluded that increased La wt. % loadings resulted in larger catalyst particle sizes (due to sintering) which in turn caused larger fiber thicknesses.

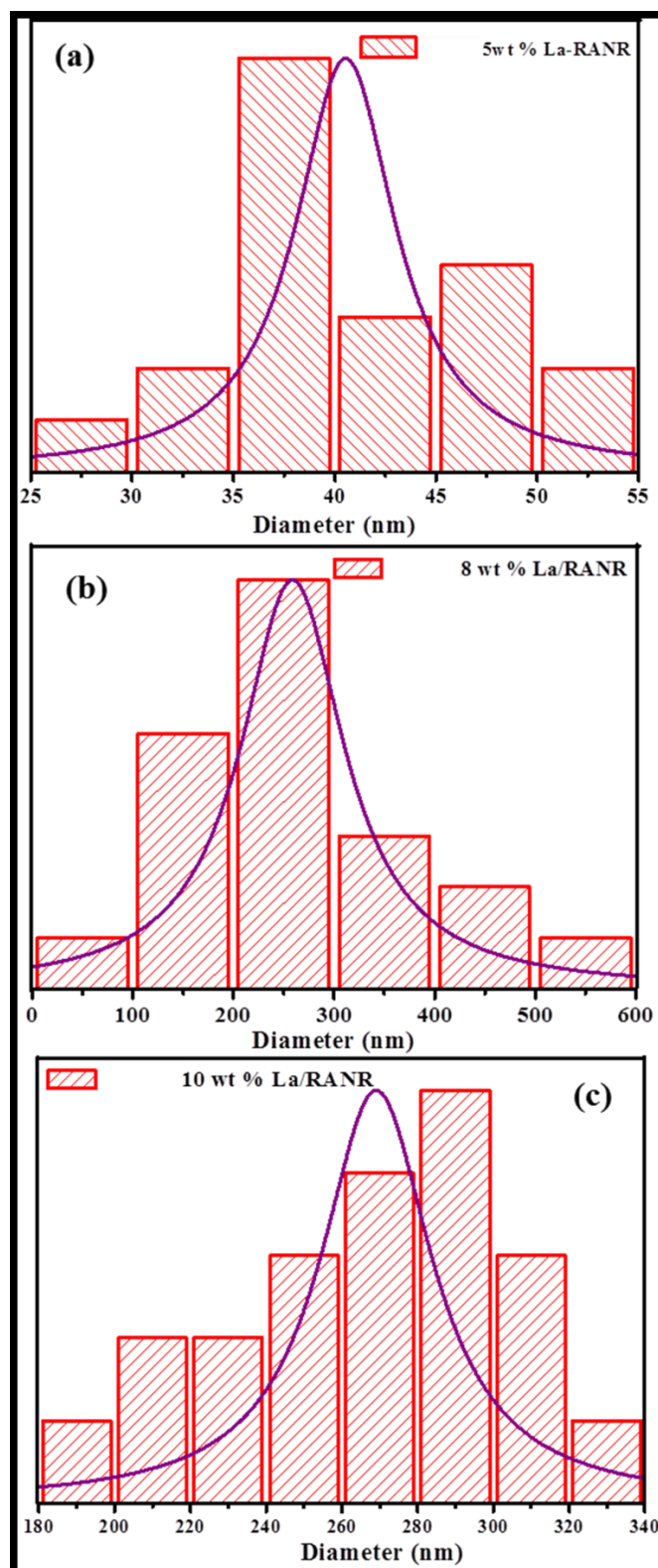


Figure 5.4 Thickness of the CNFs formed at: (a) 5 wt. % La/RANR (b) 8 wt. % La/RANR and (c) 10 wt. % La/RANR at 700 °C for 2 h and a flow rate of 100 mL min⁻¹.

The TEM micrographs in **Fig. 5.5** compared CNFs synthesised over 8 and 10 wt. % L/RANR over a 1 and 2 h reaction time interval. **Fig. 5.5(a)** and **(b)** showed CNFs synthesized at 8 wt. % La/RANR (a relatively high loading). Here the CNFs were generally characterised by large diameters (> 200 nm) and were more crystalline than those produced under a combination of lower loading, flow rate and reaction time. In particular, amorphous carbon was observed to have deposited on the surfaces of CNFs (**Fig. 5.5(b)**) when the reaction time was doubled (i.e. 1 h to 2 h). This observation was consistent with a phenomenon described by J. B. Bai *et al.* where CNFs and CNF coils, that were synthesized by CVD over alumina, were observed to have had only amorphous carbon deposited on their outer layers after long time exposures at high temperatures.³⁰ At higher temperatures and the same flow rate, the CNFs were well formed and homogeneous. However, at lower temperatures (< 500 °C) and flow rates (< 50 mL min⁻¹) there was little exposure of the catalyst, such that inconsistencies developed in sectional diameters and morphology. For instance the CNFs in **Fig. 5.5(b)** appeared deformed and inhomogeneously bent. Despite longer exposure time (i.e. 2 h) the CNFs in **Fig. 5.5(b)** grew to greater lengths with significant deformities (as confirmed by the laser Raman spectroscopy - **Section 5.4.6**).

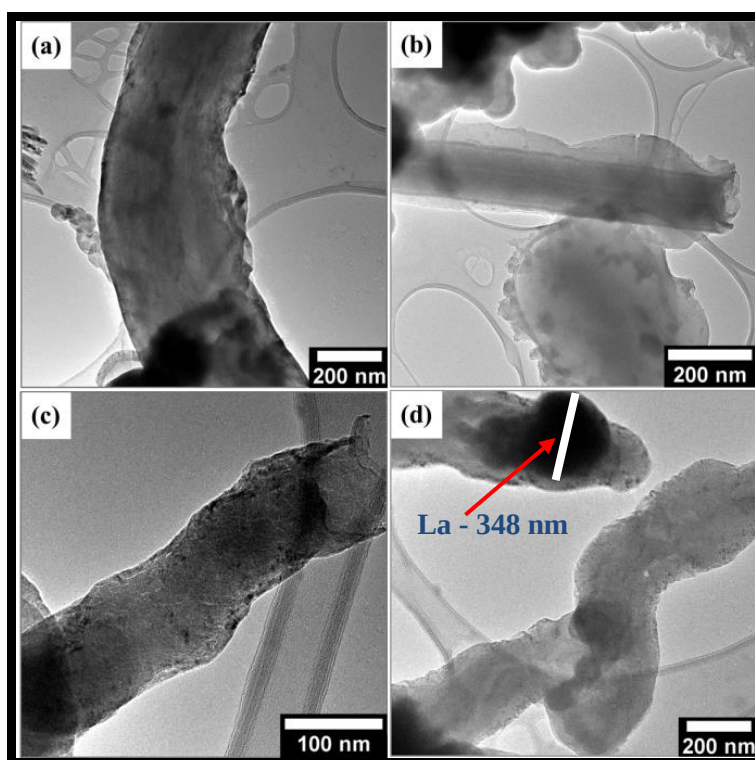


Figure 5.5 TEM micrographs of CNFs synthesised over 8 wt. % La/RANR (a) 100 mL min⁻¹ for 1 h at 700 °C and (b) 100 mL min⁻¹ for 2 h at 700 °C and 10 wt. % La/RANR (c) 100 mL min⁻¹ for 1 h at 700 °C and (d) 100 mL min⁻¹ for 2 h at 700 °C.

Fig. 5.5 (c) and (d) showed micrographs of CNFs synthesised at a higher loading of 10 wt. % La/RANR. The fibers are generally characterised by large diameters and are more crystalline than those produced under a combination of low wt. % metal catalyst loading, flow rate and short time. Hence it was tentatively concluded that the extent of graphitisation appeared to be dependent both on the reaction temperature as well as the flow rate of C_2H_2 . Similarly, it appeared that the crystallinity and fiber morphology was directly influenced by the size of the La particle. As far as it could be ascertained, this is the first reported use of La on its own as a catalyst for the synthesis of CNFs. Hence further investigation is required to get a full understanding of the general growth mechanism of CNFs from it as well as establishing the threshold conditions under which stable crystalline and more graphitic CNFs can be formed.

5.4.3 Percentage weight loading variation

The wt. % of La loaded onto the RANR support was varied to determine its effect on the nature and morphology of the SCNMs that were synthesized by this CVD method over a 1 h period. The wt. % loading of La on RANR was varied from 0.5, 1.0, 2.0, 5.0, 8.0 and 10 wt. %. TEM analyses showed that at lower wt. %. loadings (0.5, 1.0 and 2.0 wt. % La/RANR) no CNFs were formed. For instance for a 1.0 wt. % La loading on RANR, amorphous carbon was observed to have deposited around the catalyst at temperatures from 500–700 °C (**Fig.5.6**).

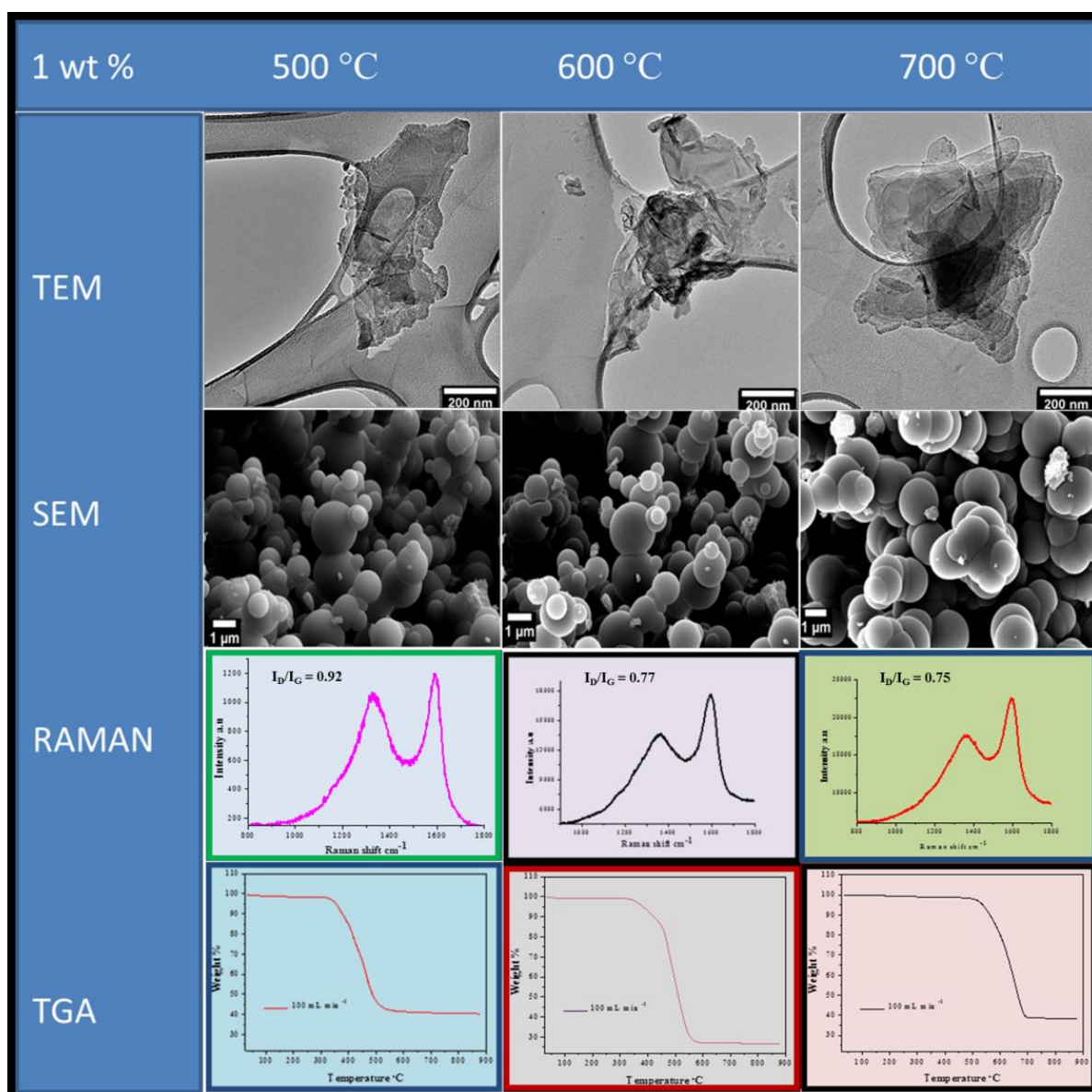


Figure 5.6 Detailed analyses of the CVD products that were synthesized over 1 wt. % La/RANR at a temperature range of 500 – 700 °C and a flow rate of 100 mL min⁻¹.

The trends presented in **Fig. 5.6** were also observed for the CVD products that were synthesized over 0.5 and 2 wt. % La/RANR. The TEM and SEM micrographs in **Fig. 5.6** showed clumps of transparent carbon materials that appeared like folded sheets (which may even have been graphene layers). The laser Raman spectroscopy (LRS) data of these materials (**Fig. 5.6**) showed that there was an increase in orderliness in the carbon matrix that formed with increased temperature (i.e. the I_D/I_G ratio decreased with increased reaction temperature). This was confirmed by the TGA profiles in **Fig. 5.6** which showed that the decomposition temperatures increased with increased reaction temperature i.e. the amount of ordered carbon materials that had formed had increased. Based upon this data it was

concluded that the catalytic activity for CNF formation at low loadings of La on RANR (i.e. between 0.5 and 2 wt. %) was negligible. Similarly it was concluded that the formation of disordered, structure-less carbon sheet-like products was as a result of pyrolysis and not catalytic transformation of C_2H_2 over La loaded onto RANR.

Conversely at 5 wt. % loading, CNFs were predominantly synthesized. TEM and SEM micrographs (**Fig. 5. 7**) revealed an increase in density coverage for CNFs that were formed around the supported catalysts as the reaction temperature was increased. This implied that a combination of moderate to high loading of La on RANR and a higher temperature promoted the nucleation and shaping of carbon into CNFs with various degrees of graphicity. This was confirmed by both LRS and TGA data as presented in **Fig. 5.7** Raman analysis showed that the G-band increased (and hence the I_D/I_G ratio decreased) as the reaction temperature was increased from 500 – 700 °C; TGA showed that the onset of the decomposition temperature increased from 400 °C to 700 °C as the reaction temperature was increased. **Fig. 5.4** showed that there was an associated increase in the average diameter and length of the CNFs with both wt. % loading of La on RANR and reaction temperature. The trends that were observed in diameters, lengths, graphicities and thermal stabilities were comparable to CNFs from other metal catalysts (**Chapters 6 – 8**) supported over RANR except their morphologies that differ due to differences in growth mechanisms supported by different. The trends presented in **Fig. 5.7 and 5.8** were also observed for the CVD products that were synthesized over 5 – 10 wt. % La/RANR at 75 mL min⁻¹ for 1 h.

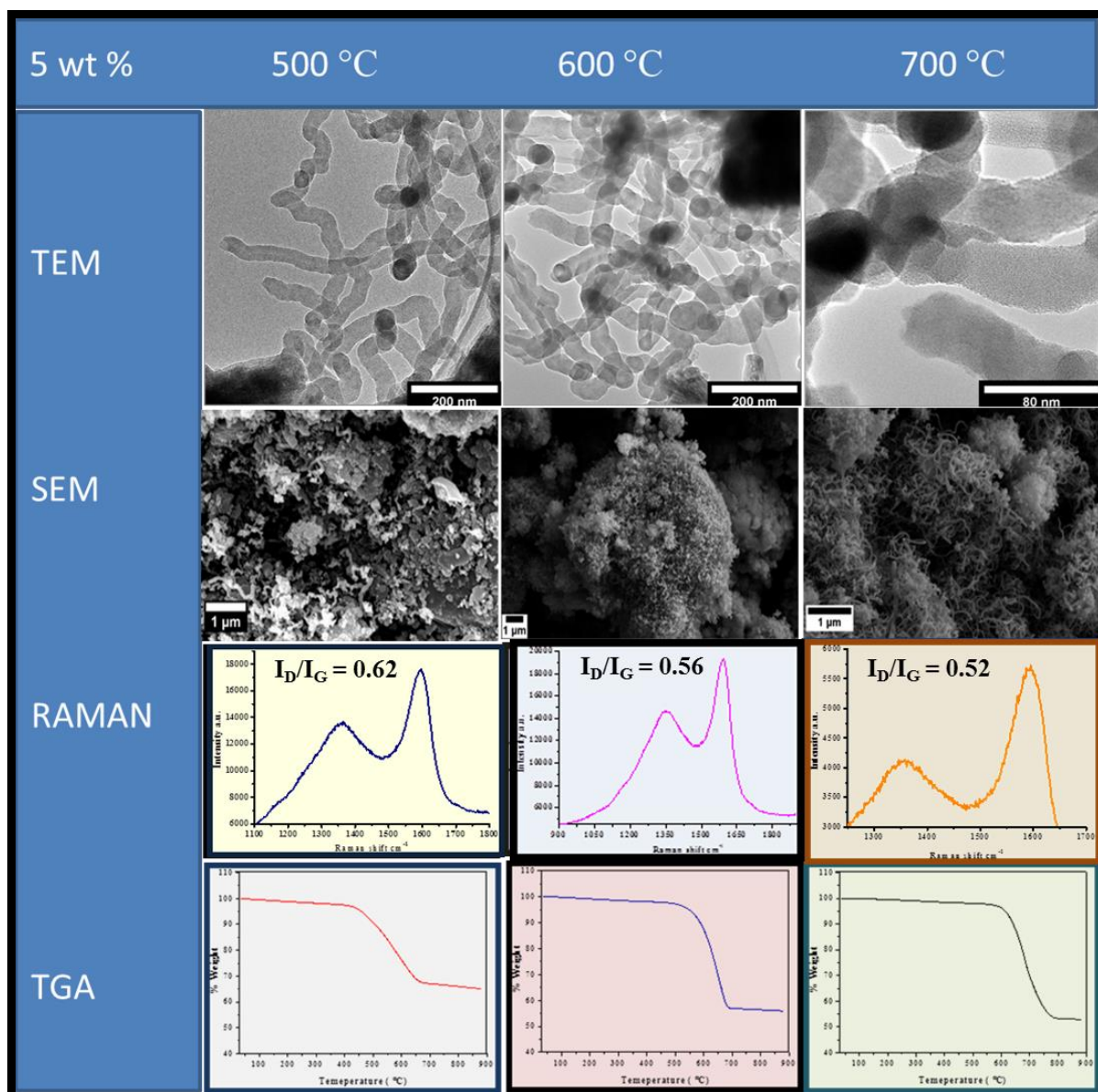


Figure 5.7 Analysis of the CVD products that were synthesized over 5 wt. % La/RANR at a temperature range of 500 – 700 °C and a flow rate of 100 mL min⁻¹ for 1 h.

When the wt. % loading of La on RANR was increased to 8 wt. % and 10 wt. % it was noted that the catalytic performance also resulted in the synthesis of CNFs. However, their performances and efficiencies were noted to be poor than that of the 5 wt. % La/RANR catalysts. Additionally it was observed that there was a significant change in the morphology of the products that were synthesized. For instance, the straight CNFs produced at 5 wt. % were mostly absent at 8 and 10 wt. %. Rather the products that formed (in both the 8 and 10 wt. %) appeared as spheres that had been joined together and were arranged into randomly bent and twisted chains (especially at lower reaction temperatures) as shown in **Fig. 5.8** The data presented in **Fig. 5.8** also represent the phenomenon observed for 8 wt. % La/RANR.

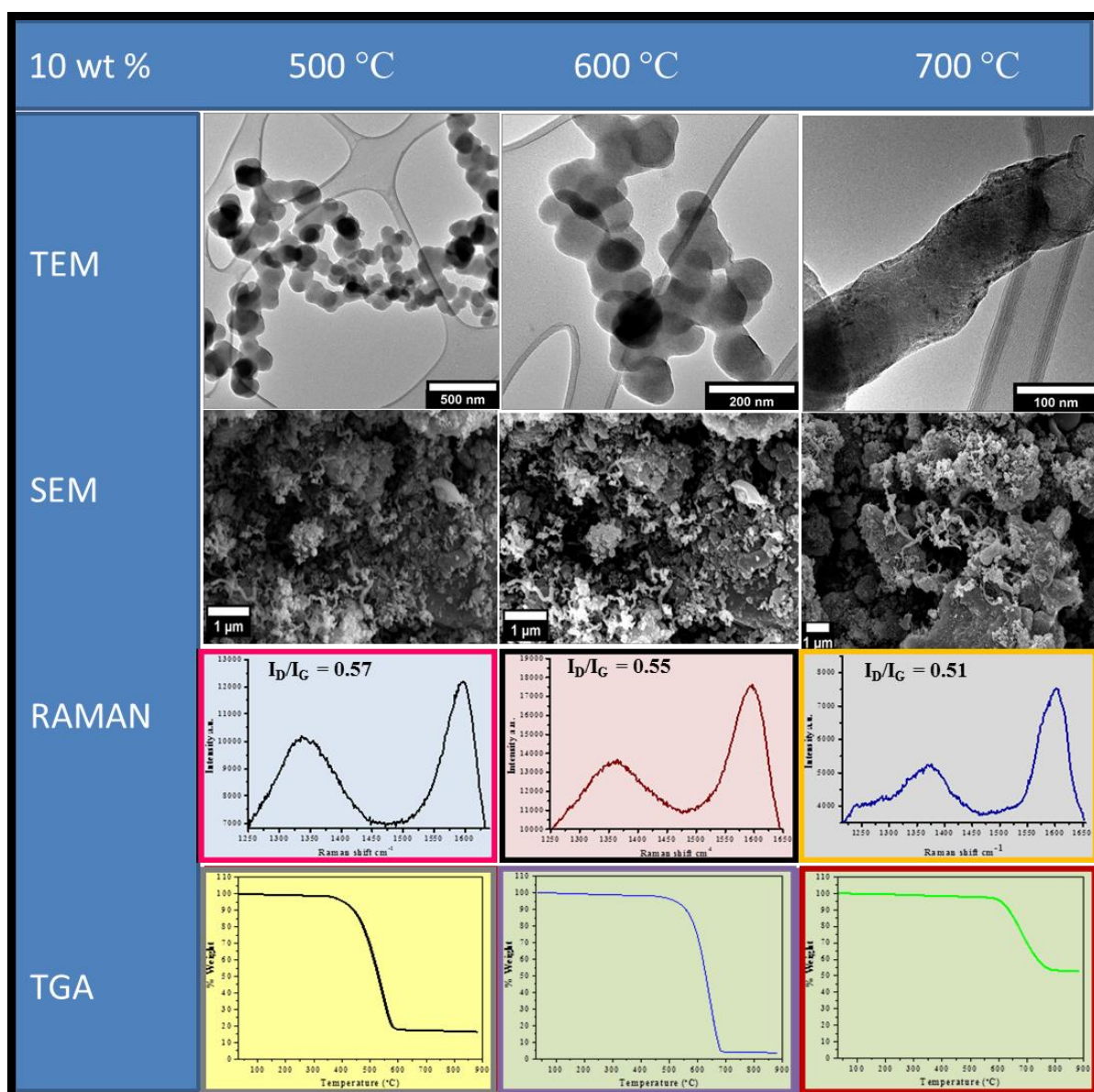


Figure 5.8 Analysis of the CVD products that were synthesized over 10 wt. % La/RANR at a temperature range of 500 – 700 °C and a flow rate of 100 mL min⁻¹ for 1 h. The micrographs shown represent the majority product in each case.

5.4.4 Gas Flow rates

In order to examine the effect of the flow rates of C_2H_2 and H_2 (the carrier gas) these were changed at 25 mL min^{-1} intervals i.e. 50, 75 to 100 mL min^{-1} . Here it was observed that the various La/RANR catalysts performed differently as the flow rates were varied. For instance at 50 mL min^{-1} , the La/RANR catalysts changed from white to a dark brown colour (carbon deposit) during the CVD reactions at temperatures between 300 and 400 °C. However, these catalysts did not catalyse the synthesis of any form of SCNMs. This was confirmed by both TEM and SEM analyses. For CVD reactions conducted at 500 to 700 °C all the catalysts turned black, but there was no significant increase thereof in the quartz boat afterwards. This showed that the La/RANR (irrespective of loading) could only sparingly catalyse C_2H_2 in H_2 at 100 mL min^{-1} into amorphous carbon layers as no SCNMs were observed (**Fig. 5.6**).

At gas flow rates of 75 and 100 mL min^{-1} it was observed that the La/RANR catalysts turned black over a temperature range of 500 – 700 °C. TEM, SEM (**Fig. 5.7 and Fig. 5.8**) and Raman analyses (**Section 5.4.3**) of the products that had formed, causing the catalysts to change colour, revealed that CNFs had been synthesized under these flow rates. In addition it was observed that highly ordered pyrolytic graphite (HOPG) had been synthesized at higher temperatures (**Fig. 5.8**) when the flow rate was 100 mL min^{-1} . This implied that the effect of having varied the gas flow rate was mainly on the conversion of C_2H_2 gas to CNFs. It was therefore concluded that as the flow rate was lowered this had lowered the conversion of C_2H_2 and hence the quantity of CNFs that were synthesized. However, the flow rate could not singly be attributed to the variation of the morphology of the CNFs that were synthesized.

5.4.5 Reaction duration

The durations in which the catalyst were exposed to the C_2H_2/H_2 mixture in the synthesis of CNFs were increased from 30 min to 1 h and then to 2 h. These different durations represented an increased exposure of the gas feed (i.e. C_2H_2/H_2) to the reaction surfaces of the various La/RANR catalysts. Here it was observed that most catalysts did not react at 30 min, even at higher wt. % loadings and moderate flow rates. However, when the flow rate was increased to 75 mL min^{-1} and the temperatures were varied between 600 °C and 700 °C then it was observed that the products which formed for the 10 wt% La/RANR catalysts, for reaction durations of 1 and 2 h, once again appeared like spheres that had been joined

together to form twisted chains (**Fig. 5.9**). These were strikingly similar to those that had previously been observed (see **Fig. 5.8** in **Section 5.4.3**).

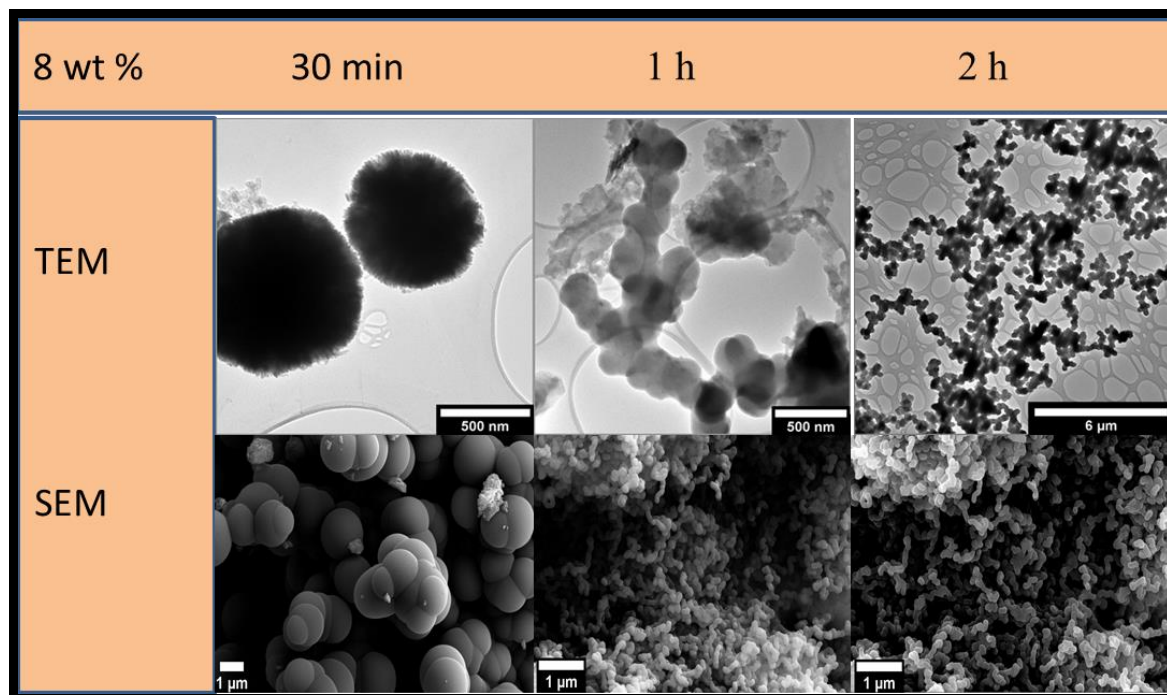


Figure 5.9 The effect of reaction duration on the CVD products that were synthesized over 8 wt. % La/RANR at a temperature of 700 °C and a flow rate of 75 mL min⁻¹.

On the other hand, when the flow rate was increased to 100 mL min⁻¹ and the temperatures were varied between 600 and 700 °C, then it was observed that CNFs were synthesized across the whole range of wt. % loadings as shown in **Figs. 5.6 – 5.8**.

5.4.6 Laser Raman spectroscopy (LRS)

One of the best ways of determining the graphitic nature of the CVD products that were synthesized over the various wt. % loadings of La on RANR was laser Raman spectroscopy (LRS). In general, LRS allows for the characterisation of various dimensions of sp² carbons including: fullerenes (0D), graphene (2D) and graphite (3D).³¹ The Raman spectra of the products where the best CNFs that had been synthesized (i.e. from 10 wt. % La/RANR catalysts in a C₂H₂/H₂ mixture at a flow-rate of 100 mL min⁻¹ for 2 h at 300 – 700 °C) were compared (**Fig. 5.10**). These Raman spectra revealed that these CNFs had a high degree of graphicity, as indicated by their narrow and less intense G-bands (**Fig. 5.10**). Equally they appeared to reveal that graphitisation of the CVD products increased uniformly with increase in reaction temperatures. This was confirmed by an I_D/I_G ratio analysis (**Table 5.1**),

seemingly as a consequence of the D and G-bands having increased proportionally in intensity with increase in reaction temperature. Even so, the considerably high intensity of the D-band in each case showed that a significant degree of disorderliness also existed in these carbonaceous products.

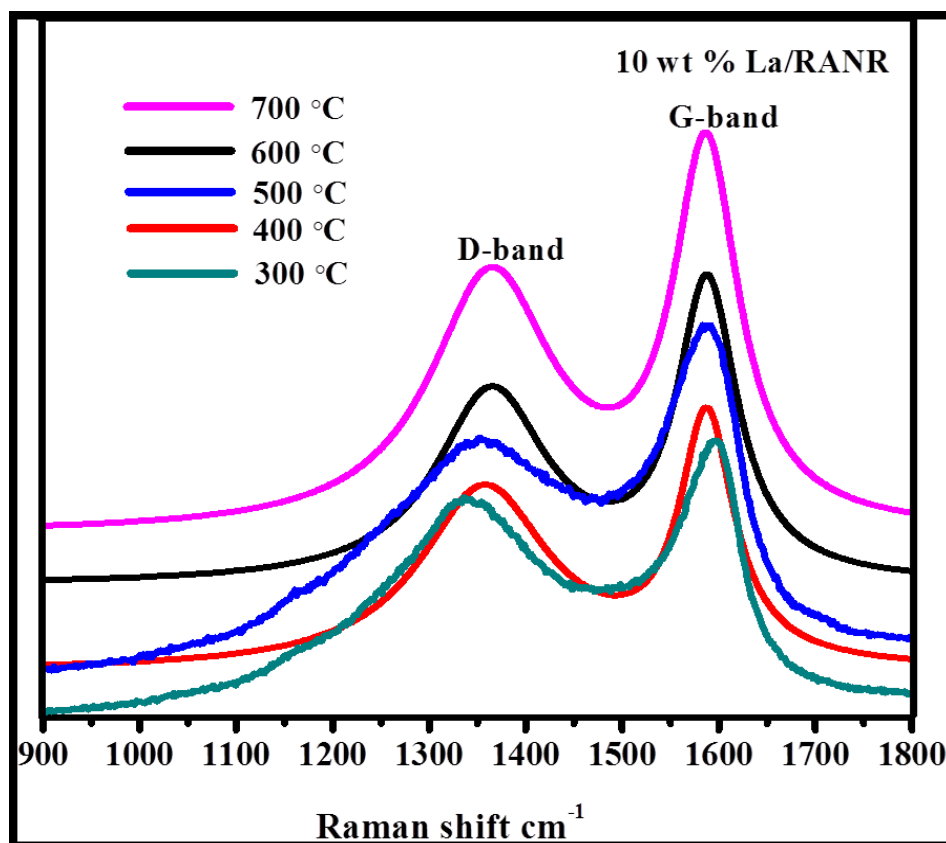


Figure 5.10 Raman spectra of CNFs synthesized by CVD over 10 wt. % La/RANR from a $\text{C}_2\text{H}_2/\text{H}_2$ mixture at 100 mL min^{-1} flow-rate for 2 h at 300 – 700 °C.

Table 5.1. LRS data of CNFs synthesized over 10 wt. % La/RANR at 100 mL min⁻¹ flow-rate for 2 h.

10 wt % La/RANR	T °C	I _D	I _G	I _D /I _G
	700	8668.23	16996.53	0.51
	600	8578.71	15597.65	0.55
	500	10210.18	17912.59	0.57
	400	12186.07	19040.73	0.64
	300	13133.12	18240.44	0.72

Fig. 5.10 shows the degree of crystallinity of the CNFs. This is comparable to the PXRD analysis presented in **Fig. 5.2(c)**. Previous studies revealed that the structure of CNFs can be explained in terms of P6₃/mmc space group arrangement.³² The packing of the carbon readily became disordered along the c-axis in the CNFs because the C-atoms within the fibrous matrix bonded strongly through sp² hybridisation and arranged in a 2D honeycomb network. The layers then stacked in a hexagonally curved crystalline structure and were bound together by van der Waals forces. It was the weakness in the van der Waals forces that prompted disorderliness in the graphite-like films.³³ **Table 5.1** showed that all the samples had comparatively high I_D/I_G ratios. This is a good measure of orderliness in the planes of the curved carbon layers in the fibers.

LRS studies were also carried out on the CNFs that were synthesized over the 5 and 8 wt. % La/RANR catalysts, which showed that graphitic CNFs were synthesized here as well (**Fig. 5.7**) especially at high temperatures and flow rates (**Fig. 5.8**). It was found that all the samples gave similar Raman spectra in terms of the shapes and position of the Raman peaks. The data presented in **Fig. 5.7** also represent the Raman phenomenon of the CNFs that were synthesized over La/RANR catalysts under different conditions (gas flow rate, time and temperature) at the same loading. They exhibited strong G-bands around the 1591 cm⁻¹ region which were attributable to the first order scattering of the E_{2g} phonon of sp² C-atoms.³⁴ Weak D-bands occurred around 1345 cm⁻¹ and were due to the k-point photons of A_{1g} symmetry. The D and G peak intensities had I_D/I_G ratios with relative values of about 0.52. This

indicated that there had been an increase in the size of the in-plane sp^2 domains and hence the CNFs had become more ordered. The highly disordered CNFs exhibit very broad Raman bands.

5.4.7 Thermogravimetric analysis (TGA)

TGA is widely used for determining the thermal stabilities of organic and inorganic materials. The technique functions by carrying out measurements of weight losses or gains with increasing temperature under an inert or reactive atmosphere. Each weight change corresponds to physical or chemical processes that take place on increasing the temperature. Thermogravimetric analysis was used to study the thermal stabilities of selected CNMs that were synthesized over different wt. % loadings of La on RANR under various flow rates. The thermal decomposition temperatures and wt. % losses of the selected CVD products are shown in **Fig. 5.11**

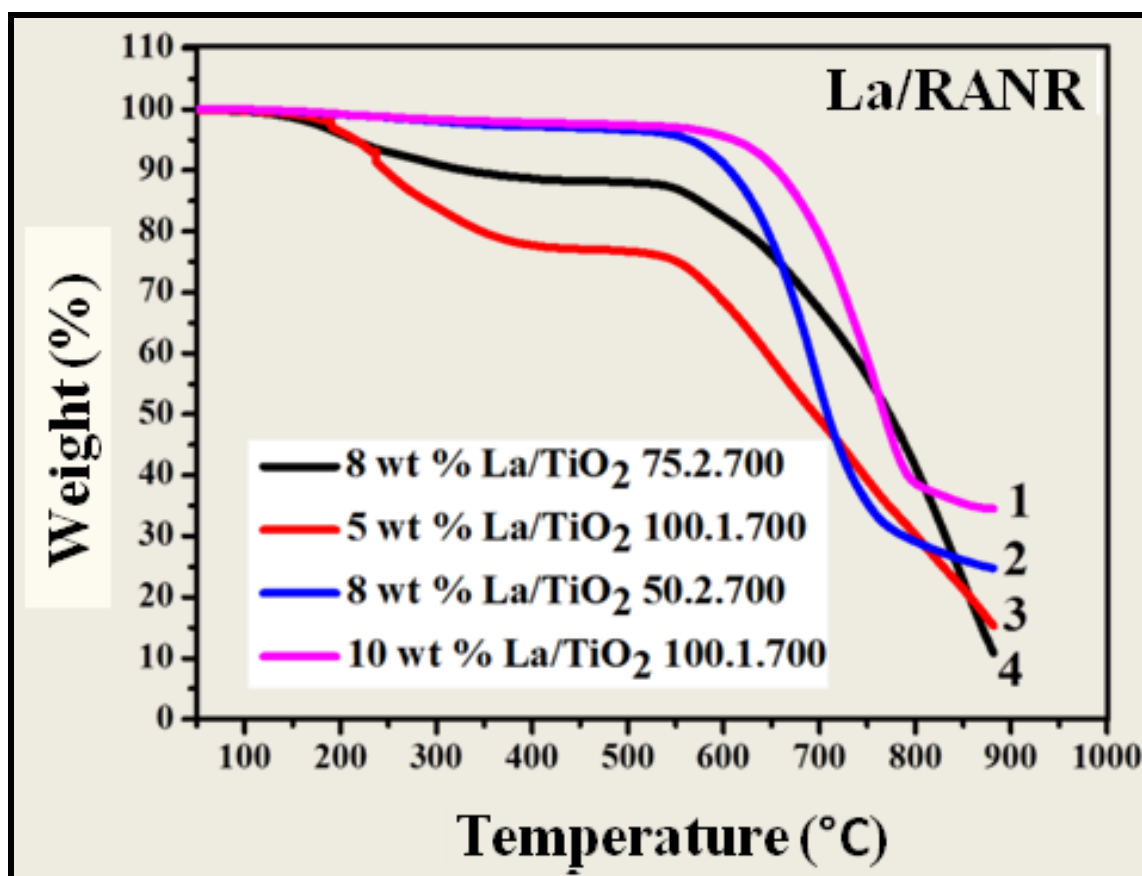


Figure 5.12. TGA analyses of the CVD products that were synthesized over various wt. % loadings of La on RANR at a flow rate of 100 mL min^{-1} for 1 h at 700°C .

Fig. 5.12 showed the decomposition patterns of the CVD products that were synthesized over the various La/RANR catalysts at uniform flow rate, time and temperature. Here it was observed that the decomposition temperature increased with increased wt. % loading of La. This implied that higher wt. % loading of La increased particle distribution over which more graphitic CNFs were synthesised. CNFs which were formed over the 10 wt. % La/RANR catalysts at 700 °C showed a decomposition temperature of 650 °C. The CNFs that were formed over the 8 and 5 wt. % La/RANR catalysts, (**Appendix D**) showed that they decomposed at 600 °C and 500 °C respectively. The amorphous carbon material that were formed over the 1 wt. % La/RANR catalysts showed decomposition temperatures at 200 and 500 °C, probably due to the presence of both amorphous carbon (i.e. at 200 °C) and graphitic carbon (i.e. at 500 °C). **Fig. 5.12** showed that the CNFs synthesized over 10 wt. % La/RANR were more stable compared to those synthesized over a lower loading of 5 wt. % La/RANR. This implied that a higher wt. % loading resulted in the synthesis of more graphitic CNFs with more highly catalytic surfaces to be more crystallised and hence exhibited greater thermal stability. The pattern in curves presented in **Fig. 5.12** supports the idea of well-knit, more crystalline and graphitic CNFs synthesised over 5 – 10 wt. % La/RANR.

Decomposition of 8 and 10 wt. % La/RANR is shown to have taken place at around 630 °C and have residual wt. % of 40 and 25 respectively. This is attributable to discontinuities in the knitting of the carbon matrix and dangling bonds by which each curved layer of the fibre walls can be unzipped and peeled away and hence characteristic higher combustion temperature than in lateral carbon materials such as graphite films (**Figs. 5.6 – 5.8**). The high temperature also improves crystallinity and hence reducing defect density and producing more graphitic CNFs.

Decomposition for 1 and 5 wt. % La/RANR in **Fig. 5.12** showed that there was presence of numerous defects along the walls and at the ends of the fibers as shown in **Fig. 5.5 (b) and (d)**. The defects resulted in instability at the edges and also consist of dangling bonds by which the fibers readily undergo thermal decomposition. Decomposition noticed on these curves ranging from 250 to 550 °C entail the presence of carbonaceous materials that desorb at the surface of the catalyst and readily combust at low temperatures. However, all curves showed that there exist residual materials that decompose beyond the TGA 900 °C temperature limit. This material may be attributed to both catalyst material and possibly temperature enhanced highly stable graphitised materials.

5.5 Conclusions

In this study it was shown that La was successfully deposited on a novel RANR support. PXRD analyses showed sharp peaks occurring at 2θ value 12° , a temperature enhanced transformation of La into a high purity phase with a hexagonal structure. It was also shown that at lower wt. % loadings of La on RANR catalysts did not catalyse the synthesis of CNFs. On the other hand, it was shown that at higher wt. % loadings of La on the RANR supports, a tip-growth mechanism was followed in the synthesis of graphitic CNFs. Based upon observations made by TEM and SEM it appeared that the size of the catalyst nanoparticles played a critical role in the control of the size and morphology of the CNFs that were synthesized. Raman analyses have also shown that these CNFs were graphitic as evidenced by their high intensity G-bands. Parametric variations of reaction conditions revealed all the possible products that could be synthesized over these catalysts. In particular it was found that the wt. % of loadings of La on RANR was paramount in the shaping of the carbon nanomaterials that were synthesized. Similarly the variation in the duration of reaction and the flow-rate of the feeder gas both appeared to influence the degree of graphitisation of the CNFs that were formed. TGA analyses showed that the La/RANR catalysts synthesized carboneaceous materials that were graphitic. It was also found that the CNFs that were synthesized over long reaction durations (i.e. 2 h) and higher flow rates (i.e. 100 mL min^{-1}) were more thermally stable and decomposed at temperatures between $600\text{-}700^\circ\text{C}$. The remaining unburnt material at 900°C was the support with catalyst.

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Chapter 6

Synthesis of twisted carbon nanofibers over nickel decorated RANR

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6.1 Introduction

Advances in nanotechnology have raised the need to synthesise nanomaterials for a wide range of applications. One such nanostructure is the CNF. CNFs exhibit high performance and their fibre architecture can be varied to meet targeted performance requirements. Detailed studies report of CNFs structural integrity and efficient load transfer from fibre to matrix in CNFs composites.¹ However, linear CNFs have limitations in their resin dominated properties such as interlaminar shear strength or longitudinal fibre compression.² Creating non-linear CNFs is one method of overcoming this. Ni is a well known catalyst for making CNFs with and without a support. Ni is also commonly known to support the synthesis of coiled CNTs.³ Manipulating this quality may enable targeted coiled or twisted CNFs that have improved shear strength and fibre compression.^{2, 3} Use of a novel structural support (RANR) loaded with Ni was hypothesized to be a method of controlling such features.³ This research seek to modify the catalytic properties of Ni by supporting it on a unique and novel RANR support in an attempt to improve the quality of the CNFs it can synthesise. This may be extended to modifications targeting non-linear CNFs with reduced interlaminar shear strength and longitudinal fibre compressions.

The catalytic performance of Ni catalysts with various wt. % loadings predominantly synthesised coiled and a few straight CNFs.³ The coiled CNFs were synthesised by the Ni metal-activated transformation at elevated temperatures of C_2H_2 and H_2 gases. The effect of wt. % loading and flow rate variation was observed to particularly play a pivotal role in determining how they influence the growth of CNFs in terms of their morphologies and dimensions. Previous studies also revealed that the larger the particle size of the Ni metal, the thicker and longer the fibers produced. These characteristics will have significant influence on the performance of the CNFs in the nano composites they form as a result of their enhanced properties.⁴

6.1 Literature review

Fibrous and tubular carbon materials can be classified by their geometric and morphological appearance. They are viewed a seamless cylinder of a rolled graphene film resulting in the formation of a single-walled carbon nanotubes or multiple nested cylinders to form multi-walled carbon nanotube.⁵ Coiling in fibrous and tubular carbon materials is described by coil

diameter and coil pitch, given by the distance between adjacent corresponding points along the axis of the helix.¹ Synthesis of carbon materials can be tailored in a wide range of macroscopic structures for various applications in the form of powders, spheres, extrudates, fibers, tubes, or honeycombs.² Applications for these materials include use as a catalyst support, novel electromagnetic wave absorber, subtle energy absorber, tuneable micro-device, bioactivator, Li battery electrode, and hydrogen and other gas adsorption and gas separation processes.⁶ Compared to straight CNFs, conduction of electricity through twisted CNFs generate an inductive magnetic field rendering the fibers more suitable for use as electromagnetic nano-transformers and nano-switches, or alternatively as high performance electromagnetic absorbers and in-plane nano interconnectors.⁵ Previous studies reported on the growth of regularly micro-coiled carbon fibers with high reproducibility by the Ni-catalysed pyrolysis of acetylene containing a small amount of sulphur or phosphorous impurity. The preparation conditions, morphologies, growth mechanism and characteristic properties of the micro-twisted carbon fibers were studied in detail.⁷

Chen, Y *et al.* discovered that reaction temperatures influence the preparation of carbon coils during Ni-catalysed pyrolysis of acetylene by significantly affecting their coil diameters. The diameters of the CNFs are affected by using sulphur as a promoter.⁸ Previous studies reported on how twisted carbon materials were obtained from Ni catalyst powders of different particle sizes. Particle sizes below 50 nm formed fibers with coil diameters of 4-5 μm . At the same particle size range, fibres, coiling at a diameter of 0.5-0.6 μm were produced with the Ni catalyst dispersed over a graphite substrate. Similarly, Ni catalyst powders of particle size 500 nm produced CNFs with coil diameter of 5 μm while Ni particles of size 5 μm produced CNFs of coil diameter 2-8 μm .⁹ Preparation of micro-coiled carbon fibers takes precedence over linear fibers because micro-coiled carbon fibers have better toughness and elasticity than linear carbon fibers and they can also be used as reinforcements to improve the strength and toughness of structural material and can also be used as minisprings and minisensors. Micro-coiled carbon fibers are a kind of chiral material that are characterised by electromagnetic cross-polarising and can possibly serve as microwave absorbing materials.³ However, the performance of carbon fibre composites can be limited by resin dominated properties such as interlaminar shear strength or by longitudinal fibre compression.¹⁰

The characteristic curvature in catalytically grown twisted carbon materials is likely to occur without a very large elastic strain.¹¹ This may be attributed to the proposed polygonisation in the tubular or fibrous carbon material and consist of short straight segments. The coiling

resulted from the introduction of pentagon-heptagon pairs at regular distances in the hexagonal network forming the wall of a straight carbon fibre.¹² Different mechanisms have been used to explain the growth of twisted carbon materials. One growth mechanism was suggested to take place on a catalyst particle at a molecular level using the heptagon-pentagon construction by which the formation of curved nanotubes, tori or coils of tubes has the same diameter as that of tubes synthesized over 20 min. Longer time exposure did not result in tubes with higher diameters. However, the number of graphitic layers might depend on the flow rate of acetylene at the catalyst particle. Thus the catalytic particle influences only the internal diameter of the coils.¹³

In this study, Ni catalyst particles with average diameter of 4 nm were dispersed on RANR support by a deposition precipitation method (DPU). The wt. % loading on the RANR was varied and the catalysts were used to synthesise twisted CNFs in a parametric study. Time, temperature and gas flow rate were varied during the catalytic decomposition of acetylene in a chemical vapour deposition (CVD) reaction. The influence and effect of varying the reaction conditions on the morphology of the twisted microstructures and their dimensions and their growth mechanism was investigated. A comparative study was conducted on the catalytic performance of Ni on different types of support. An intrinsic understanding of how nanocoils were formed and a proposal for the growth mechanism for these microstructures in relation to the parameters of the reaction conditions was attempted.

The mechanism of the catalyst-support interaction is described in terms of how TiO_2 undergoes excitation at elevated temperatures forming hole-electron pair.¹⁴ This induces the reductive decomposition of C_2H_2 as the electrons generated on the surface of TiO_2 are transferred to the metallic Ni particles. The electrons are then used to reduce C_2H_2 and decompose it into carbon and hydrogen gas. Rutile TiO_2 makes its electrons available to Ni metallic particles at the catalyst-support interface. The Ni attract the electron charge and hold it at the surface of the metallic particles, avoiding the recombination of the $\text{h}^+ - \text{e}^-$ species, promoting the formation of the C atomic species used in the making of CNFs.¹⁵

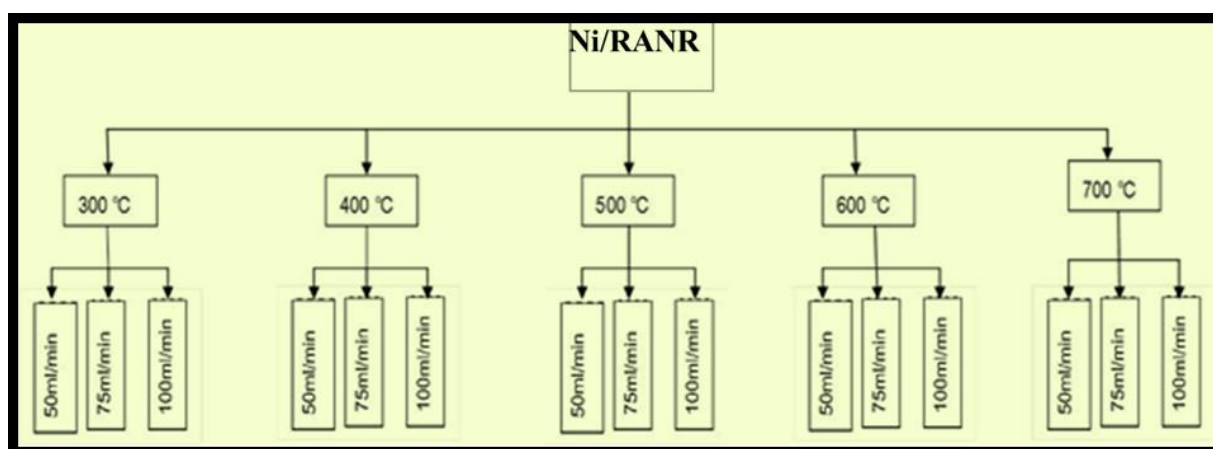
6.2 Experimental procedures

6.2.1 Preparation of the catalyst

Preparation procedure for the Ni catalysts supported on RANR was via a hydrothermal method carried out at 200 °C. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and TiCl_4 was obtained from Sigma Aldrich. The deposition–precipitation method using urea (DPU) was used to load the Ni metal onto RANR with different loadings. The catalysts were prepared using the method explained in **Section 4.3.2 in Chapter 4**.

6.2.2 Synthesis of twisted CNFs

Twisted CNFs were prepared in a horizontal quartz tube reactor in which 0.5 g of the Ni/RANR catalyst was placed in a quartz boat positioned at the centre of the furnace as presented in the set up in **Fig. 1**. The reactor was heated in a tubular furnace to temperatures ranging from 300 – 700 °C for each set of reaction parameters. The $\text{C}_2\text{H}_2/\text{H}_2$ gas mixture at a ratio of 1:1 (v/v) was introduced into the tube reactor at a flow rate of 50 – 100 mL min^{-1} for each set of reaction condition parameters. The reaction was maintained at the set reaction conditions for time periods from 30 min – 2 h. After the reaction, the furnace was allowed to cool to room temperature under H_2 . **Scheme 1** outlines the parameters and the variables used in the parametric study.



Scheme 1. Flow-diagram of the parametric study for the preparation of SCNMs from Ni/RANR at different wt. % loading.

6.2.3 Characterisation of catalysts and CNFs

The fine yellow powder catalyst samples collected after centrifugation and drying were analysed using powder X-ray diffraction (PXRD). This was used to determine crystallographic phases of the catalyst particles on a Bruker D2 Phaser diffractometer in a 2θ range from 7° to 120° using $\text{Co K}\alpha$ radiation.

The morphology and material dimensions such as particle sizes of catalyst particles, diameters of the CNFs and the as-synthesised CVD products were determined by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). For TEM analysis, the samples were prepared by dispersing a small amount of the materials in methanol with slight sonication. The drops of the dispersed material were placed on a Cu micro-grid. A FEI Spirit operated at a voltage of 120 kV was used. For SEM analysis, the samples were directly mounted on a carbon tape on a sample holder stub. A FEI SEISS FIB was used for SEM observation. The average particle size was determined using ImageJ and statistical analysis of TEM and SEM micrographs. A minimum of 200 particles were measured on the TEM micrographs using ImageJ software.

Energy-dispersive spectroscopy (EDS) analysis of the chemical composition of the carbon nanomaterials and catalyst materials was performed using the TEM FEI Spirit 120 kV. Thermogravimetric analysis (TGA) of the supported catalysts and the carbon materials was performed to determine the thermal stability of these materials. This was supplemented by temperature programmed reduction (TPR) analysis of the precursor catalyst material and the as-synthesised CVD carbon materials. Raman spectroscopy has been used to characterise the sp^2 carbons from 0 to 3D such as 3D graphite, 2D graphene, 1D carbon nanotubes, and 0D fullerenes. The 1D and 2D laser Raman spectroscopy data was used to explain the crystallographic nature of the carbon nanomaterials synthesized in this work.

6.3 Results and discussion

6.3.1 Effect of RANR support on Ni in the Ni/RANR catalyst

Preparation of the supported catalyst was done by loading Ni nanoparticles onto a RANR support using the DPU method as explained in **Section 3.1.3**. The effectiveness of the

Ni/RANR as a catalyst is due to the success of DPU method of catalyst loading that give Ni particles with a homogeneous particle size distribution on the RANR nanorods and hence a close interaction with the RANR support. **Fig. 6.1** shows a PXRD pattern of 10 wt. % Ni/RANR with Ni and rutile phases distinctively represented. The Ni-RANR support interaction was observed to be a simple surface support with no Ni-Ti-O phases formed as shown in the PXRD patterns presented and explained in **Section 4.4.3** and **Fig. 3** in **Appendix A**.

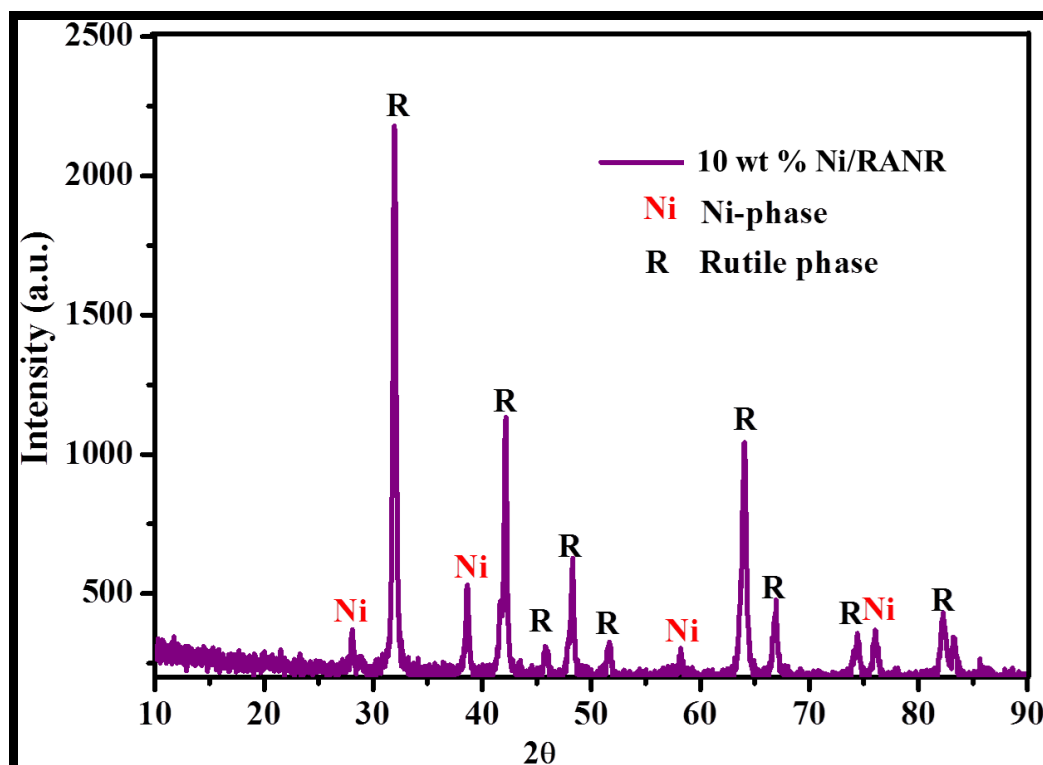


Figure 6.1 PXRD pattern of supported 10 wt. % Ni/RANR support catalyst calcined at 700 °C for 4 hr.

Fig. 6.2 shows SEM and TEM micrographs of the plain RANR and the Ni/RANR catalyst. The insert in **Fig 6.2(b)** shows the diameter distribution of the RANR nanorods on which Ni nanoparticles are supported. Detailed analysis showed that the RANR nanorods have a diameter range of 2-12 nm with an average diameter of 7 nm. The assembling of the TiO₂ nanorods into a 3D RANR nanostructure (**Fig. 6.2(b)**), presents steric hindrance such that Ni particles of large sizes do not fit between the rutile nanorods. As the Ni metal remain in solution, decrease in the metal concentration renders the particles more soluble. The gradual increase in pH as urea continues to decompose precipitates and deposit Ni on the RANR support as particles of very small size (**Fig. 6.2(c)**).

The insert in **Fig 6.2(c)** shows the particle size distribution of the Ni in the Ni/RANR catalyst. The Ni particles have a size range 1-6 nm and average particle size of 4 nm. The RANR support helped prevent sintering of the Ni by providing more nucleation sites on the RANR support and hence less agglomeration tendencies while the particles are kept sparsely distributed on the nanorods of the RANR support. The RANR morphology also increase the ion-exchangeable ability between the metallic species and consequently increases the catalytic activity and performance of the supported Ni nanoparticles.

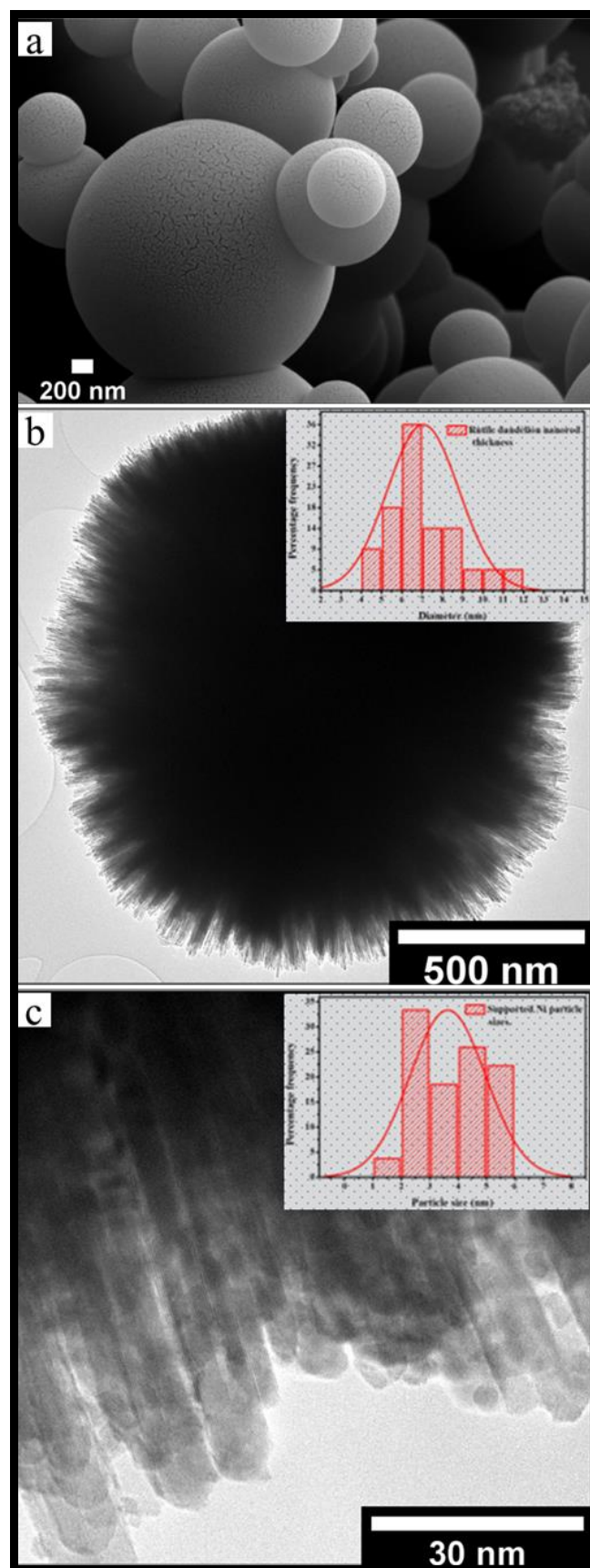


Figure 6.2. (a) SEM micrograph of plain RANR, (b) TEM micrograph of a plain RANR and (c) TEM micrograph of a 5 wt. % Ni/RANR.

The distribution of the Ni metal particles also affected the density and coverage of the CNFs formed around the catalyst as shown in **Fig. 6.3(a) – (d)**. This influenced and affected the diameter of the CNFs synthesized over the catalyst. It is apparent that the RANR are an actively interactive support that enhances the catalytic performance of the Ni metal nanoparticles on its surface in the synthesis of CNFs. The growth of the CNFs on the supported catalysts is however subject to reaction parameters. Variation of wt. % loading, reaction temperature, gas flow-rate and reaction time can have a significant effect on the morphology, mechanical properties and density of the CNFs grown via the CVD method of synthesis.

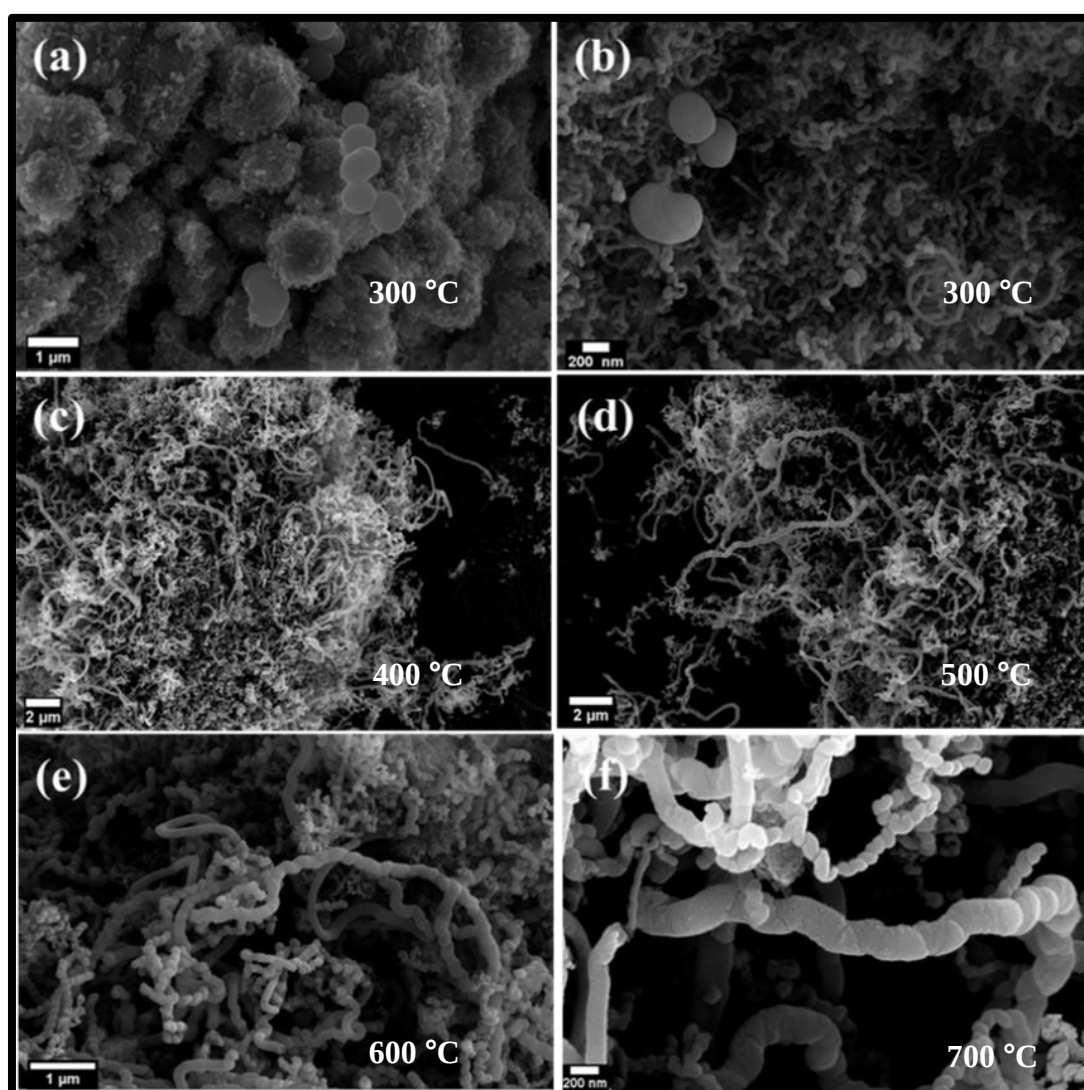


Figure 6.3 SEM micrographs of twisted CNFs grown on 10 wt. % Ni/RANR at 100 mL min⁻¹ for 2 h.

The micrographs in **Fig. 6.3(a and b)** shows uncovered catalyst and a dense network of twisted CNFs synthesized over a 10 wt. % Ni/RANR at 100 mL min⁻¹ for 2 h. **Figs. 6.3 (c) and 4(d)** shows twisted CNFs prepared under same conditions, but at different temperatures. The density of the twisted CNFs is higher around the 400 – 700 °C than at temperatures less than 700 °C. The CNFs exhibit similar properties and characteristics (long in length, mean diameter ranging from 200-250 nm, average coil pitch and coil diameter).

6.3.2 Effect of time

CVD allows growth of carbon nanomaterials at low temperatures. Even with the lowest gas flow rates attainable, growth time in the CVD method of synthesis is critical in determining mobility of carbon atoms. At short time periods, there is a formation of non-hexagonal C-rings and consequential bending, branching, ring-closing, plane-buckling or coiling due to the introduction of pentagon-heptagon pairs in the hexagonal framework of a nanoscale fibrous matrix (**Fig 6.3** and **Fig. 6.6**). This phenomenon gives rise to coiling in both CNTs and mostly in CNFs. Twisted CNFs are synthesized by regular oriental nucleation of heptagons and pentagons along the nanofibre body.⁵ **Fig 6.3(a)** shows fibers clustered around individual Ni/RANR. The fibers were synthesized at different set of reaction conditions.

The micrographs in **Fig 6.4** showed some uncovered catalyst particles. This was attributed to a very short time period of catalyst exposure to the carbon sources. CNFs growth time is thus a crucial parameter that can be used to understand the growth process and tailor the inherent simulated properties of the resulting carbon material assembly.¹⁰ It can thus be inferred that there is a threshold set of reaction conditions over which growth of fibers is consistent and also time required to achieve uniform coverage.

Figs. 6.4 – 6.6 present the effect of reaction time on the CNFs synthesised over different time periods at a temperature range of 300 – 700 °C, over 5 wt. % Ni/RANR at a flow rate of 100 mL min⁻¹. Detailed studies on CNFs synthesised over 1, 8 and 10 wt. % Ni/RANR showed similar trends with time at various temperatures, wt. % metal loading and flow rates. The 0.5 wt. % Ni/RANR did not catalyse the synthesis of twisted CNFs except to form some amorphous carbon deposited on the catalysts. The figures presented TEM and SEM data complemented with Raman profiles showing a systematic increase in the G-band, with increase in temperature. However, **Figs. 6.5** and **6.6** show that at longer synthesis time periods, graphitisation increases with time. Temperature is thus not the only factor affecting the degree of graphitisation in the CNFs produced.

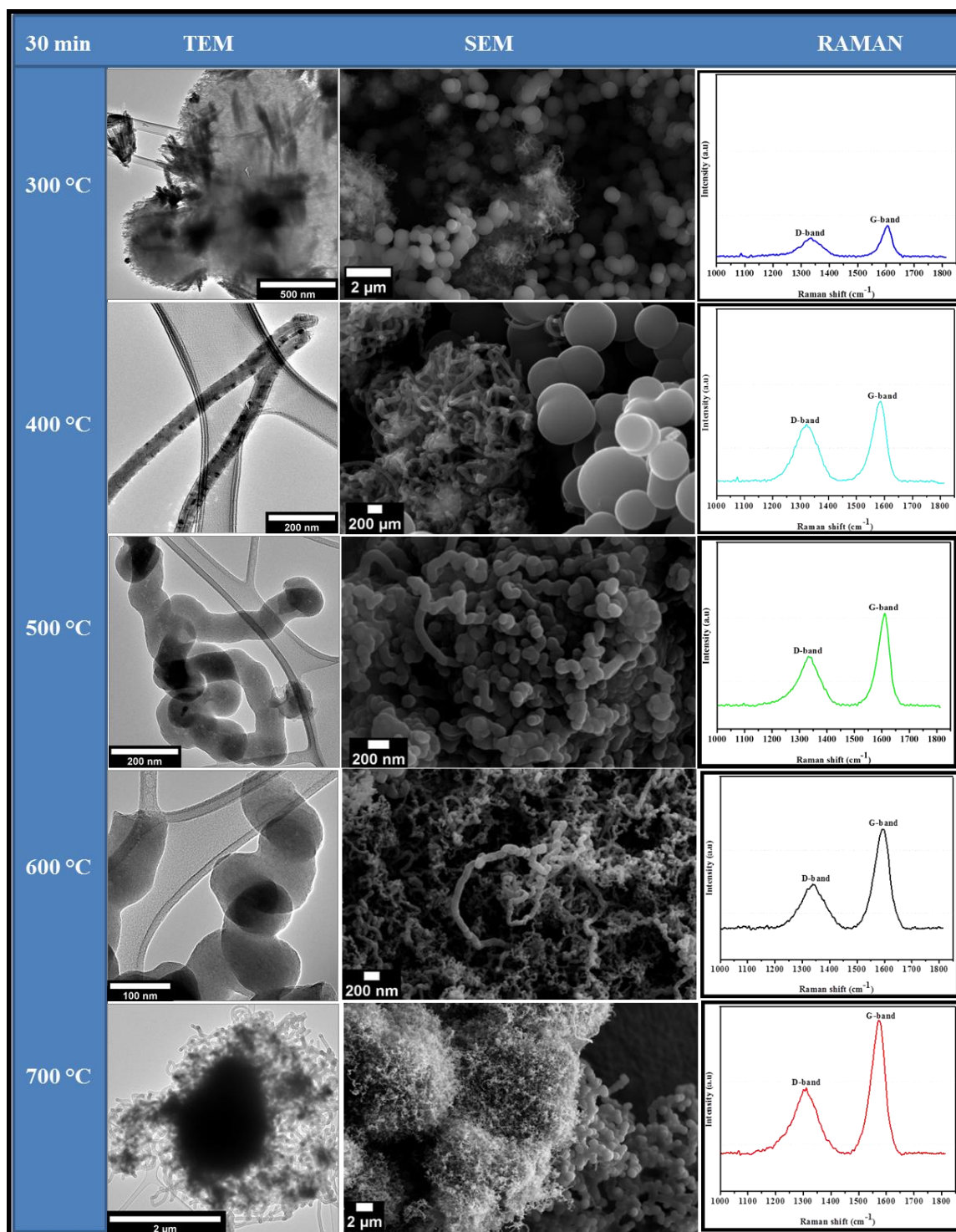


Figure 6.4. Twisted CNFs synthesized over 5 wt. % Ni/RANR at 30 min period and a flow rate of 100 mL min⁻¹ comparing time as a factor affecting CNFs growth at different temperatures.

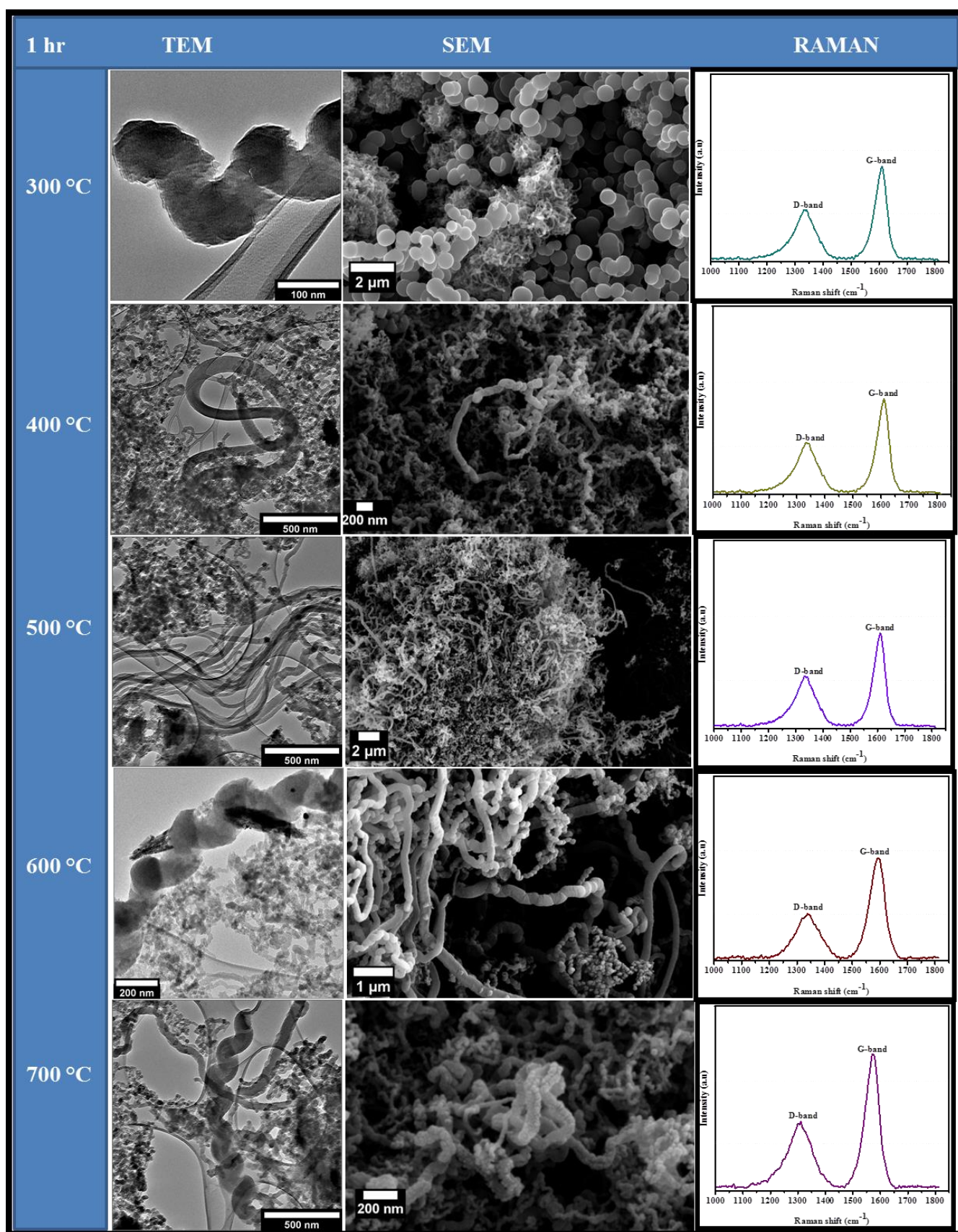


Figure 6.5 Twisted CNFs synthesized over 5 wt. % Ni/RANR at 1 h period and a flow rate of 100 mL min^{-1} comparing time as a factor affecting CNFs growth at different temperatures.

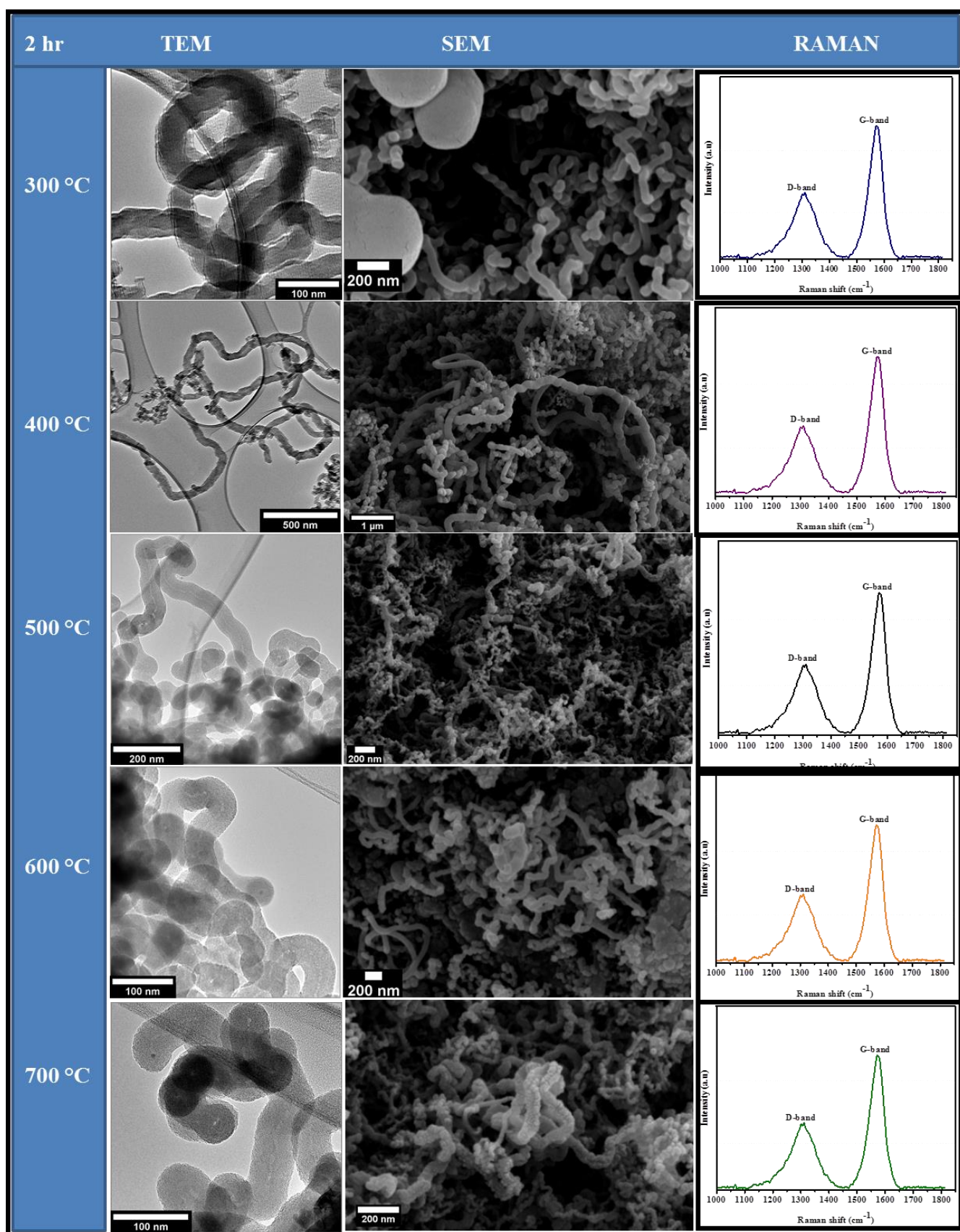


Figure 6.6 Twisted CNFs synthesized over 5 wt. % Ni/RANR at 1 h period and a flow rate of 100 mL min⁻¹ comparing time as a factor affecting CNFs growth at different temperatures.

Detailed analysis also showed that the density of CNF network increased with increase in synthesis time. It was also observed that the degree of twisting and coiling in the CNFs increased with increase in time and temperature as shown in **Figs. 6.5 and 6.6**. This implies that a longer time period enables the carbon dissolved in the catalyst to be synthesized into a more ordered carbon framework shaped into CNFs.

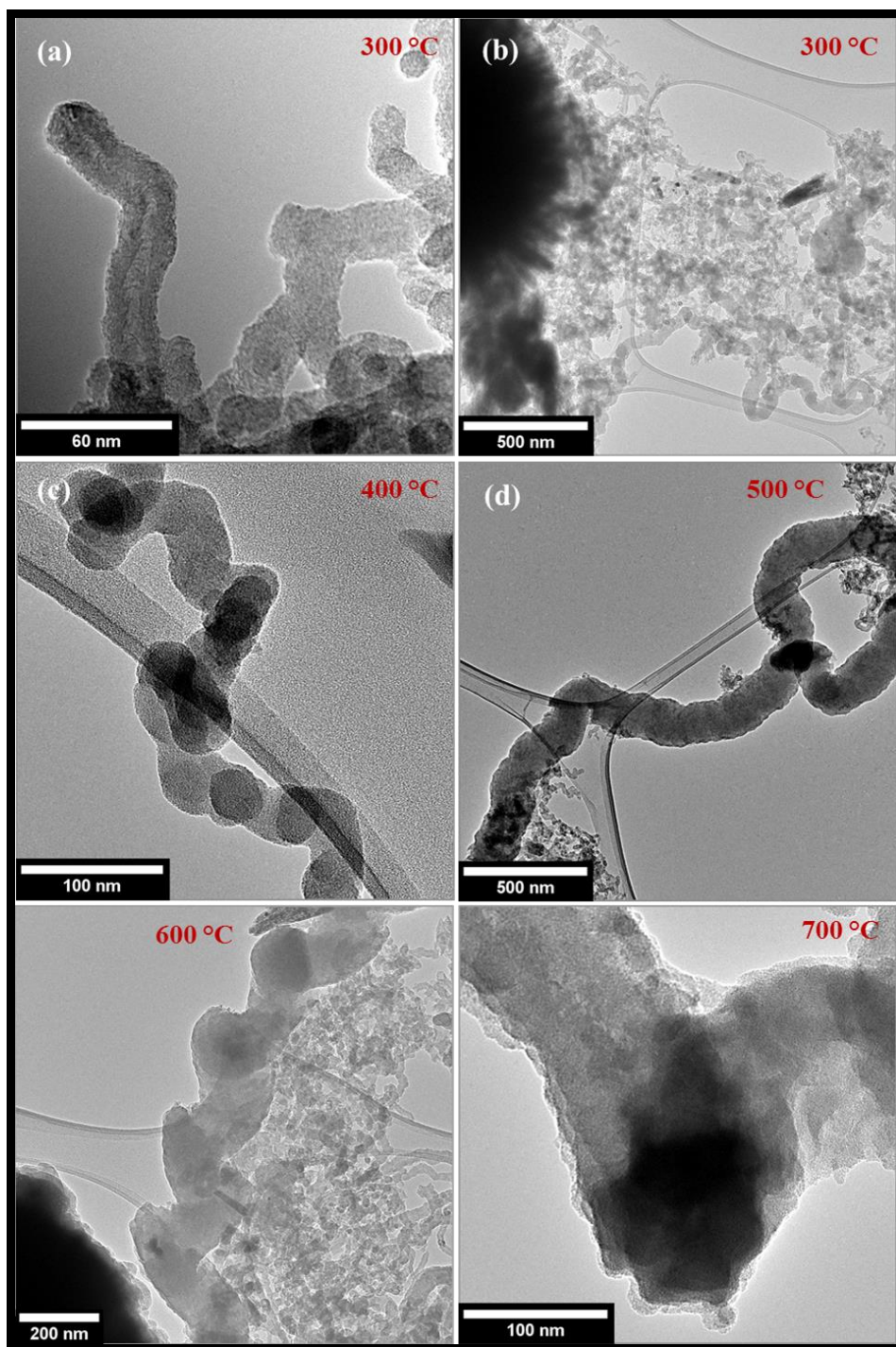


Figure 6.7. TEM micrographs of twisted CNFs on 10 wt. % Ni/RANR at 100 mL min⁻¹ for 2 h.

CNFs grown at different temperatures also showed differences in length. **Fig 6.7 (a and b)** presents short and thin fibers while those in **Fig. 6.7 (c) – (f)** showed thick and long fibers. It was postulated that though fibers would have been grown at different temperatures, they did maintained a more consistent length at 1 h and 2 h than the disordered fibers grown at higher temperatures but very short time of 30 min. These trends are largely consistent with the enhanced flow rate and kinetics of the decomposing C_2H_2 for the CNF's growth. This is also a demonstration that with sufficient time, uniform coverage similar to that obtained for systems with deposited catalyst directly onto the support surface can be obtained.¹⁶

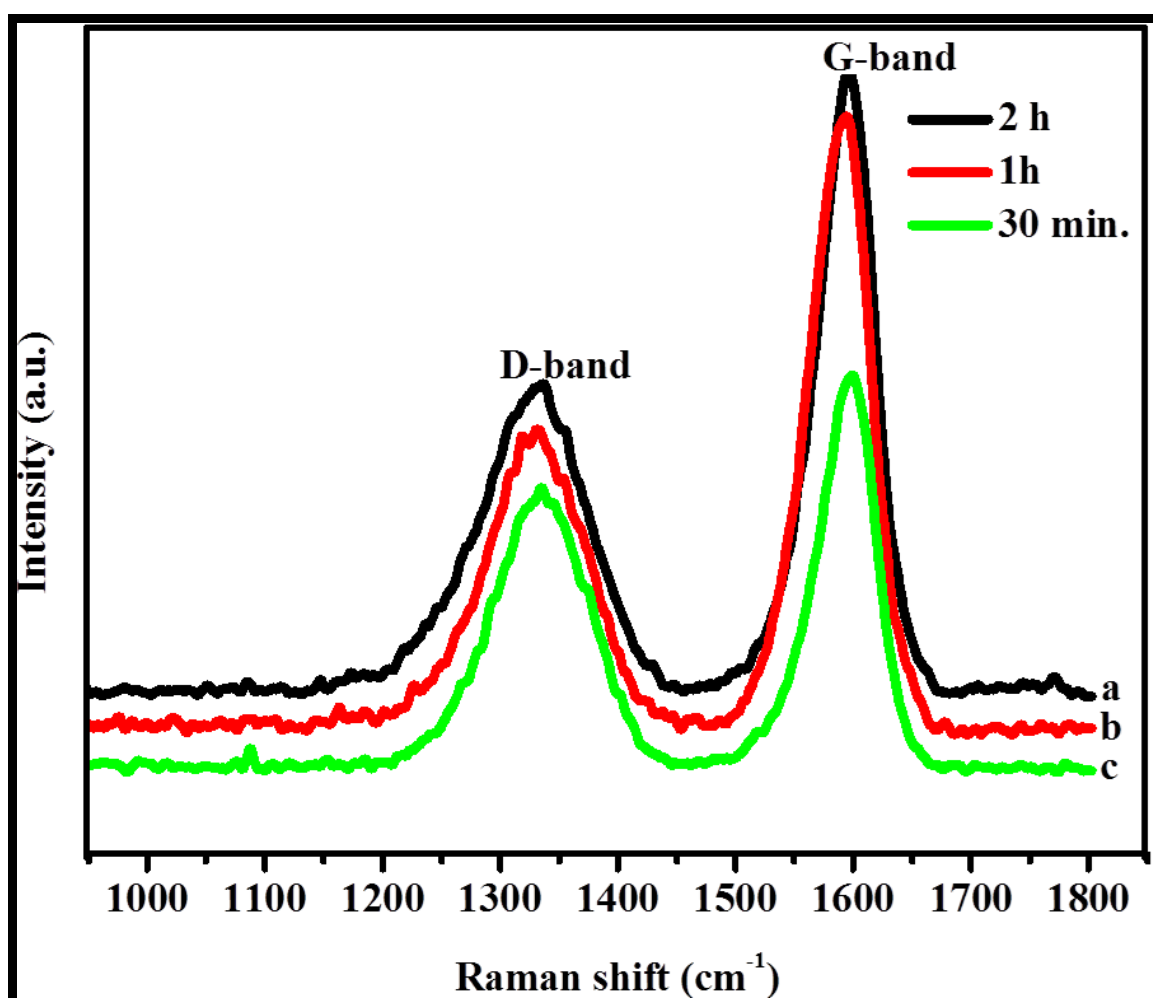


Figure 6.8. Raman spectra of CNFs over 10 wt. % Ni/RANR synthesized at (a) 2 h, (b) 1 h and (c) 30 min at 700 °C, 2 h, and 100 mL min⁻¹.

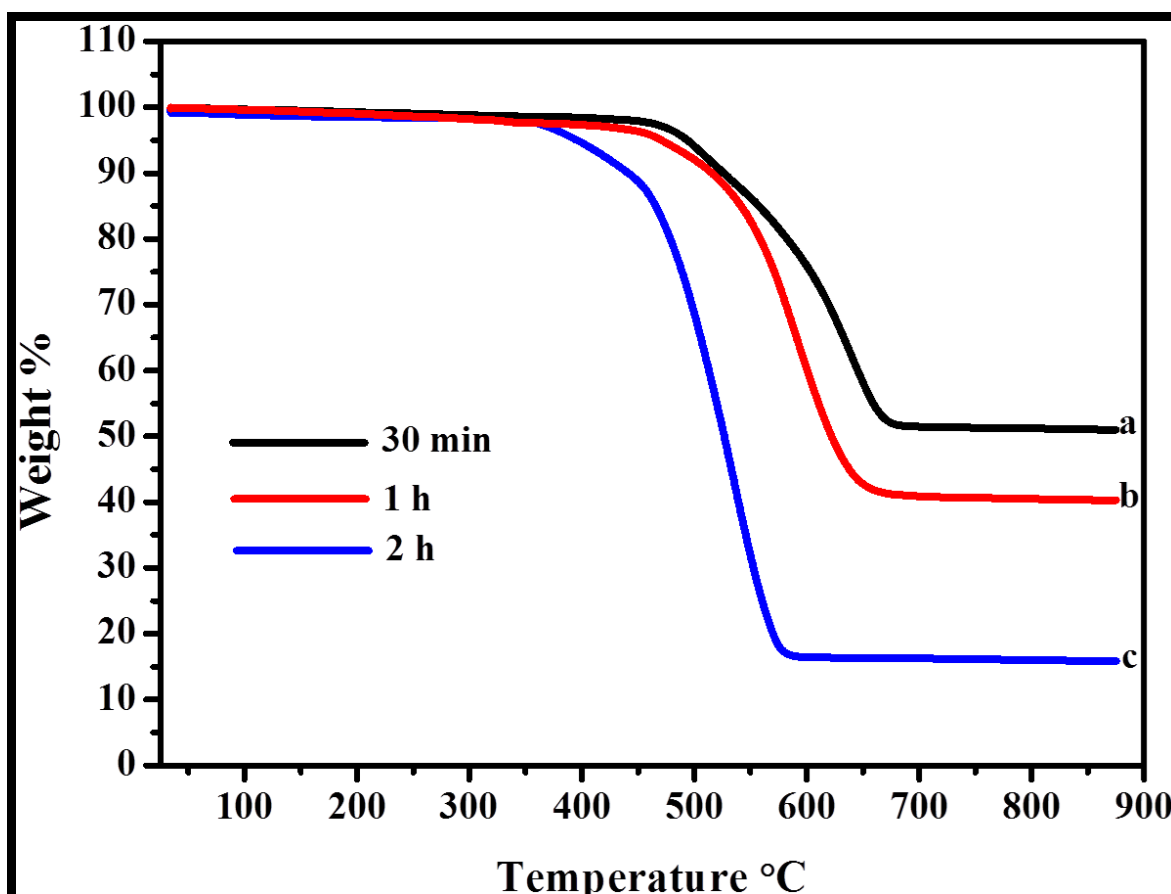


Figure 6.9. TGA spectra of CNFs over 10 wt. % Ni/RANR synthesized at (a) 2 h, (b) 1 h and (c) 30 min at 700 °C, 2 h, and 100 mL min⁻¹.

Time variation has a direct effect on the degree of graphitisation in the CNFs prepared by CVD synthesis method. **Fig. 6.8** shows that the longer the time, the more graphitic the CNFs are. The G-band in spectrums of **Fig. 6.8 (a)** and **6.8 (b)** are higher than in **6.8 (c)** which is at 30 min. High wt. % loading and temperature do not give rise to an increase in graphiticity of the CNFs. The D-band at all the respective time intervals showed uniform intensity. This shows that the carbon crystallisation on the catalyst result in the formation of amorphous carbon. Sufficient heating effect will then transform the carbon into graphitic material while the catalyst shapes the carbon material into its specific morphology. Thus longer time exposure coupled with moderate to high temperatures, allows amorphous carbon material to transform into a more ordered graphitic form of the synthesis products. It can be concluded that the time variation set traceable trends in the synthesis of twisted CNFs using CVD method. Thus at short time periods and low temperatures, there are no CNFs synthesized (**Appendix D**). However, at short time periods but high flow-rates and high temperatures, short fibers with a micropore are formed (**Figs 6.6 and 6.7 (a)**). At longer time periods, thick

solid and long length fibers are formed irrespective of wt. % loading or temperature. **Fig. 6.9** shows how temperature affected and modified the structural and mechanical properties of the twisted CNFs. The TGA curves in **Fig. 6.9** shows that decomposition of the CNFs took place at higher temperatures (**Fig. 6.9 (a)**) and a lower residual wt. % loss of the materials. This is attributed to lower density CNF coverage due to the short time of synthesis. However, slightly lower temperature was observed for decomposition of materials synthesised over a 2 h period (**Fig. 6.9 (c)**). This is a modification brought about by temperature variation which promoted structural changes in the crystalline CNFs. However, higher temperatures also gave rise to materials characterised by the presence of amorphous carbon material as shown in the Raman spectra (**Fig. 6.10**), that show broad based D peaks of considerably high intensities.

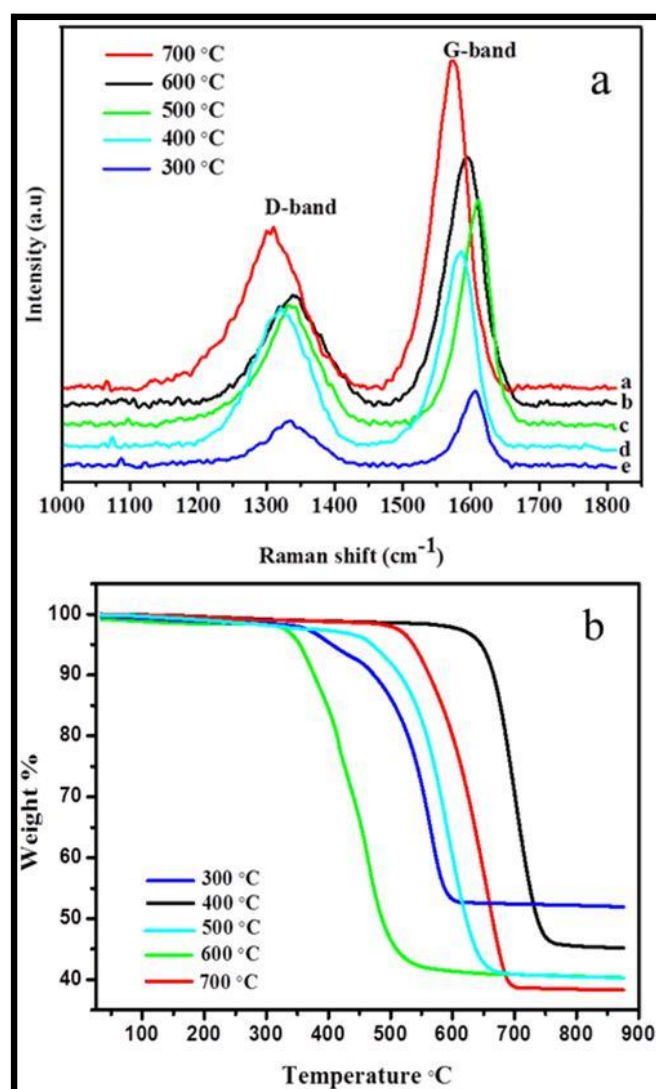


Figure 6.10 (a) Raman spectra and (b) TGA profiles of 8 wt. % Ni/RANR-CNFs synthesised at 300 - 700 °C, 2h and 100 mL min⁻¹.

The G – peak is sharper and narrower showing that temperature is contributing towards increasing graphitisation in the CNFs. It can be concluded that around 600 °C the CNFs decompose and undergo complete oxidation to gaseous products. The observed increased weight loss at both longer time periods (**Fig. 6.8**) and high temperature (**Fig. 6.9**), coupled with higher flow rates, may be due to enhanced growth at these conditions that tend to support growth of more crystalline CNFs which are denser and thicker than those at lower flow rates and temperatures.

6.3.3 Effect of Ni loading

The characteristic morphology of twisted CNFs depends on the nature or form of the Ni used as a catalyst. Ni has been catalytically used in the form of Ni plate,¹⁷ fine Ni powders or as nanoparticles dispersed on various types of supports.^{18, 19, 20} Previous research has revealed that the microstructure of the twisted fibers is knit around the Ni catalyst particle. **Fig 6.7 (d)** confirms what M. Kawaguchi *et al.* postulated when they observed that some of the twisted CNFs were formed by the crossing of two primary coils which grew in the same direction from a diamond-like or polyhedral-shaped Ni particle.²¹ K. T. Lau *et al.* observed that the metal nanoparticles were found in various shapes at the tips of nanotubes for the growth of twisted nanotubes and concluded that the tube growth could occur by the tip-growth model.⁵ This observation was also made in this work as shown by TEM analysis of CNFs synthesized over Ni/RANR catalysts. The Ni particle on the tip of most twisted carbon fibre served as a seed for their growth. The opposite planes in the Ni particles are crystallographically equivalent whereas adjacent planes are not. The different crystal planes result in distinct catalytic performance for the growth of the twisted carbon fibers.²¹ During the catalytic decomposition of acetylene, two carbon fibers grow in opposite direction from each pair of planes of the Ni particle. The carbon fiber strands consequently braided and intertwined with each other in a curvature corresponding to the diameter of the coils (**Figs 6.5 and 6.6** SEM micrographs at 700 °C). This phenomenon can be attributed to differences in growth rate and flow rate of the C₂H₂/H₂ gas mixture.

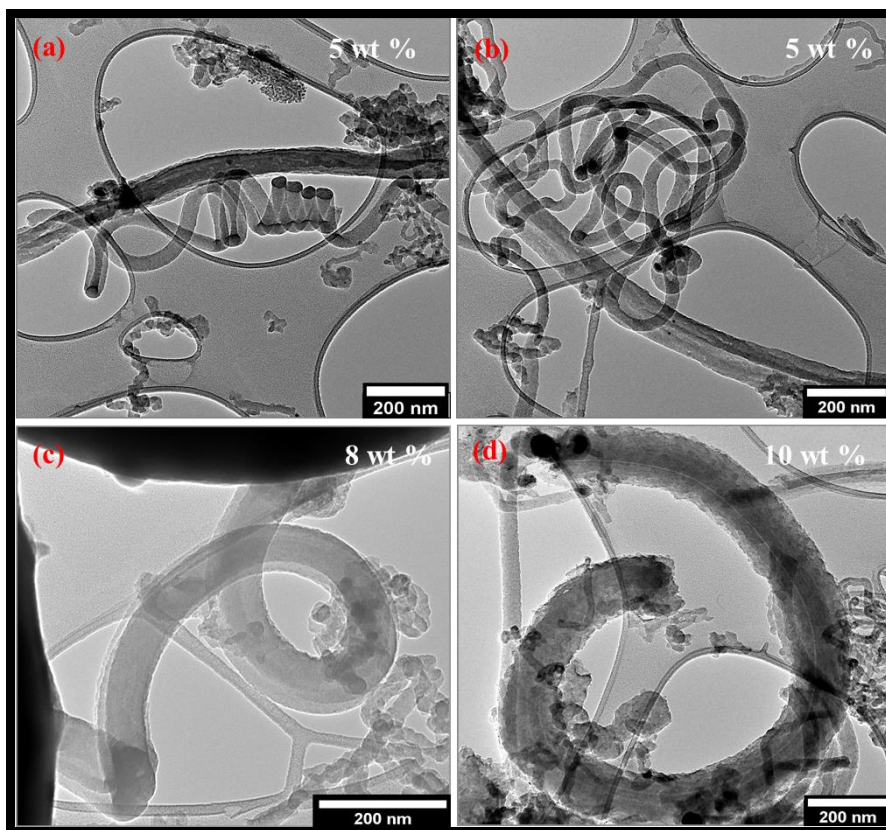


Figure 6.11. TEM micrographs of CNFs synthesised at 600 °C, 1 h, 75 mL min⁻¹ (a) and (b), 5 wt. % Ni/RANR (c) 8 wt. % Ni/RANR (d) 10 wt. % Ni/RANR.

However, **Fig 6.11** shows braiding of two or more primary coils that grew in the same coiling direction from a diamond-like or polyhedral geometric Ni particle (**Fig. 6.7 (b) and (d)**). The Ni particle size determines the properties of the twisted CNFs. This includes coil diameter, the pitch and the twisted CNF's diameter. **Figs. 6.7 (d) and (f)** showed thick fibers with high coil diameters (about 200 nm). This coiling is explained in terms of the carbon catalysed pyrolysis mechanism by which Ni is the catalyst of carbon deposition and condensation. The carbon atoms obtained from decomposition of acetylene dissolved into the catalyst grain and condensed from different crystal planes of the Ni catalyst.^{22, 4, 23} However, this growth mechanism is not uniform for all the Ni crystal planes because fibre synthesis at adjacent crystal planes takes place at different rates with respect to increasing carbon condensation and hence a resultant coil-shaped fibre.^{24, 25} The size and quality of the twisted CNFs is then influenced by wt. % loading of the Ni/RANR and the corresponding particle size of the Ni nanoparticles. The thickness of the fibers is proportional to the diameter of the Ni nanoparticle over which it grows (**Fig. 6.11 (c)**). However, varying wt. % loading did not

affect the particle size distribution on the support but particle density as proved by narrow particle size ranges across the entire wt. % loading (**Section 4.4.2**).

Fig 6.12 showed the thermal stabilities of the CNFs synthesized over different wt. % catalysts. The decrease in residual weight with an increase in wt. % Ni loading showed that CNFs density and coverage increased with increase in wt. % loading. The lower wt. % loaded catalysts seem to have catalysed more crystalline CNFs because carbon was used mostly for fabricating crystalline fibers while at higher wt. % loading, the carbon is mostly used to make primary carbon fibers which are less crystalline and less graphitic over dense activated catalyst surfaces. Detailed SEM and TEM studies revealed that at higher Ni wt. % loading on the support, catalyst distribution increased on the support and consequently resulted in a high fibre density and coverage on the Ni/RANR catalyst (**Figs. 6.2 (c), 6.2 (d), 6.3 (e) and 6.11 (d)**). It can be inferred that the lack of control on the specific particle size of the Ni nanoparticles diminishes the probability of manipulating the diameters of the twisted CNFs synthesized. **Fig. 6.3 (f)** and **Fig. 6.11 (c) – (d)** showed fibers of different range of diameters synthesized on the same catalyst. The fibers are characterised by different sizes with diameters ranging from 2 – 200 nm with an average diameter of 22 nm and wide ranging coil pitch, coil diameter and lengths averaging 500 nm.

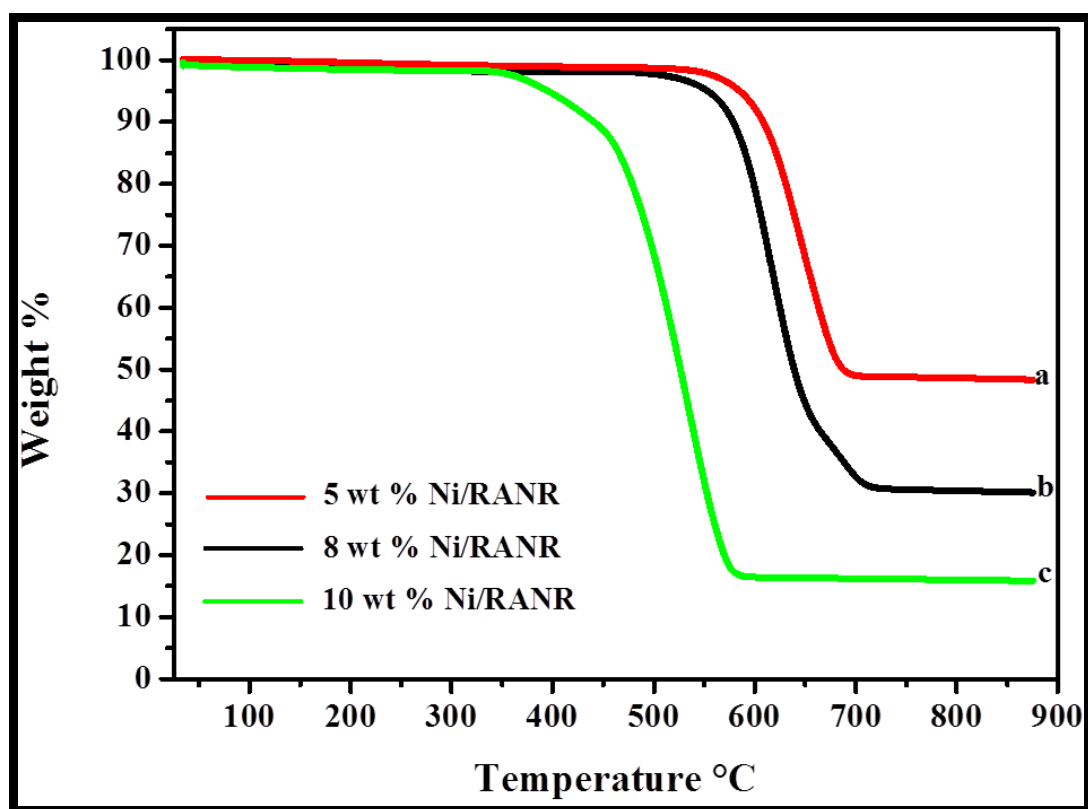


Figure 6.12 TGA of CNFs synthesized at 600 °C over 1 h period at 75 mL min⁻¹ on catalyst of the Ni wt. % loadings: (a) 5 wt. % Ni/RANR(b), 8 wt. % Ni/RANR and (c) 10 wt. % Ni/RANR.

6.4.4. Influence of flow rate on CNF formation

The flow rate of the C₂H₂/H₂ gas mixture determines the C-concentration dependence of the CVD reaction and its consequential kinetics with respect to C₂H₂ conversion into shaped carbon nanomaterials. Detailed analyses using SEM and TEM revealed that the carbon supply due to levels of flow or concentration of C₂H₂ determines the number of catalyst particles in contact with the gas and activated for the carbon nanomaterials growth (**Fig. 6.2 (c)**).

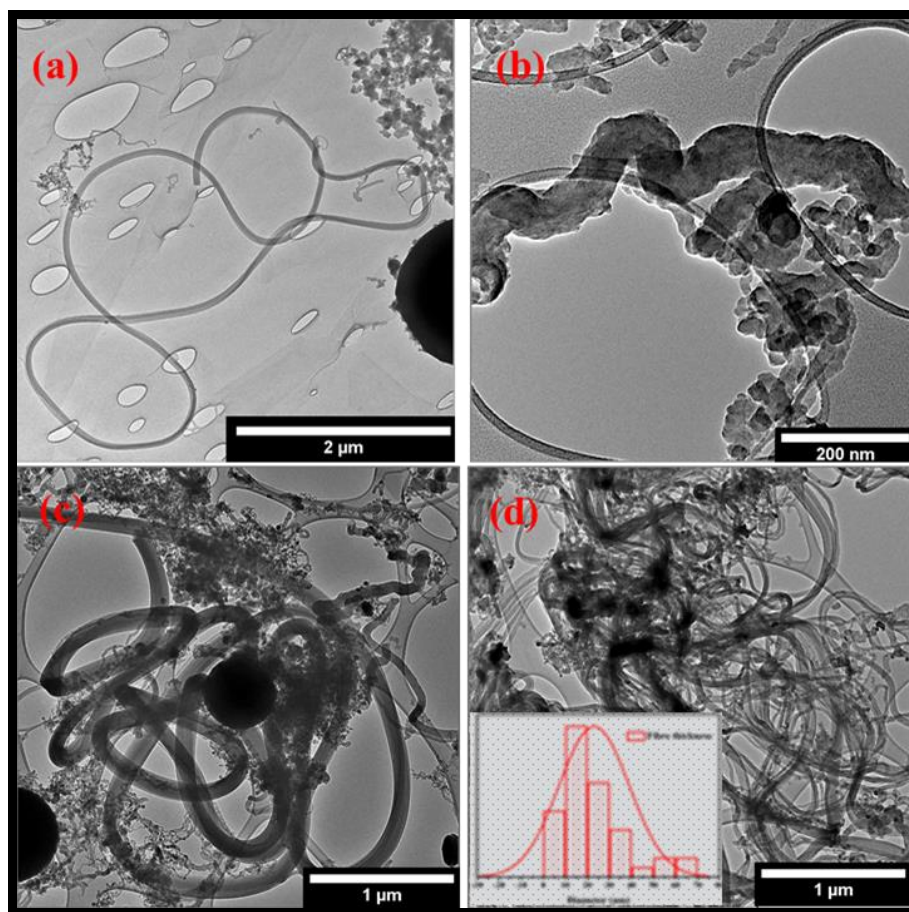


Figure 6.13 TEM micrographs of CNFs on (a) 8 wt. % Ni/RANR, 1 h, 75 mL min⁻¹, (b), 8 wt. % Ni/RANR, 1 h, 100 mL min⁻¹ (c) 8 wt. % Ni/RANR, 1 h, 50 mL min⁻¹ (d) 8 wt. % Ni/RANR, 1 h, 75 mL min⁻¹.

The lower the flow rate (50 mL min^{-1}), the less the C_2H_2 molecules were available for CNF growth. Consequently, the CNFs produced are less graphitic with D and G-bands almost of the same intensity. The observed I_D/I_G ratio for the CNFs synthesized at 50 mL min^{-1} is 0.49 and it decreased with increase in flow rate (**Fig. 6.14**). At lower flow rates, the CVD products are characterised by short CNFs with less coverage and density around the RANR supported catalyst as shown in **Figs. 6.3 (a)** and **6.4**. The CNFs became longer in length and had more coverage and high density with increase in flow rate.

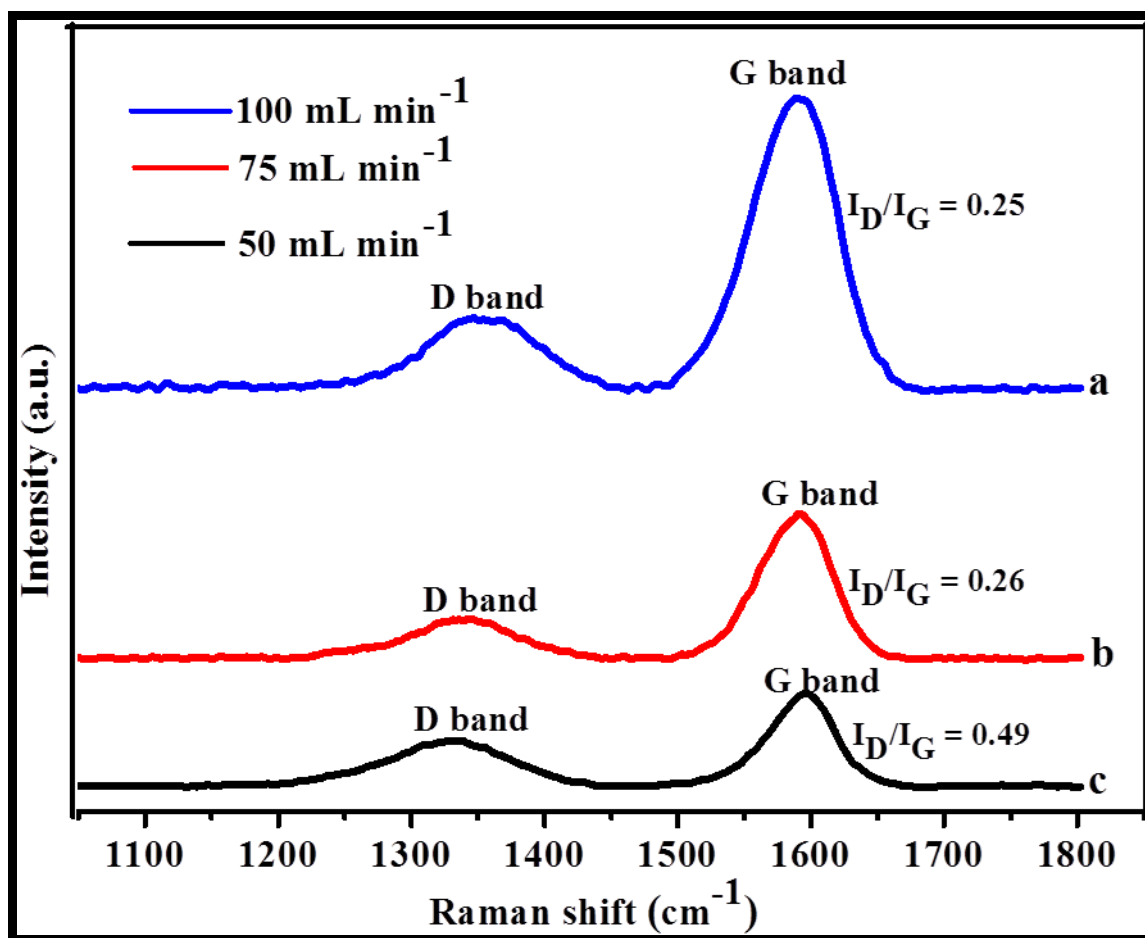


Figure 6.14 Raman spectra of CNFs on 5 wt. % Ni/RANR for 1 h and 500°C at (a) 100 mL min^{-1} (b) 75 mL min^{-1} and (c) 50 mL min^{-1} .

At higher flow rates (100 mL min^{-1}), there is observed increase in the CNFs density of high quality, more graphitic, longer in lengths, tightly wound with lower coil pitches and reduced coil diameters characterised by more regularity in their coiling (**Figs. 6.3 (f)** and **6.7 (f)**). X Chen *et al.* observed that the growth patterns of the carbon coils considerably depend on the C_2H_2 flow rate as it directly affect the deposition patterns of the carbon on the Ni catalyst

active sites.⁷ At higher flow rates, the twisted CNFs produced have a tendency to be thicker and hence a bigger diameter as compared to those synthesized at lower flow rate.

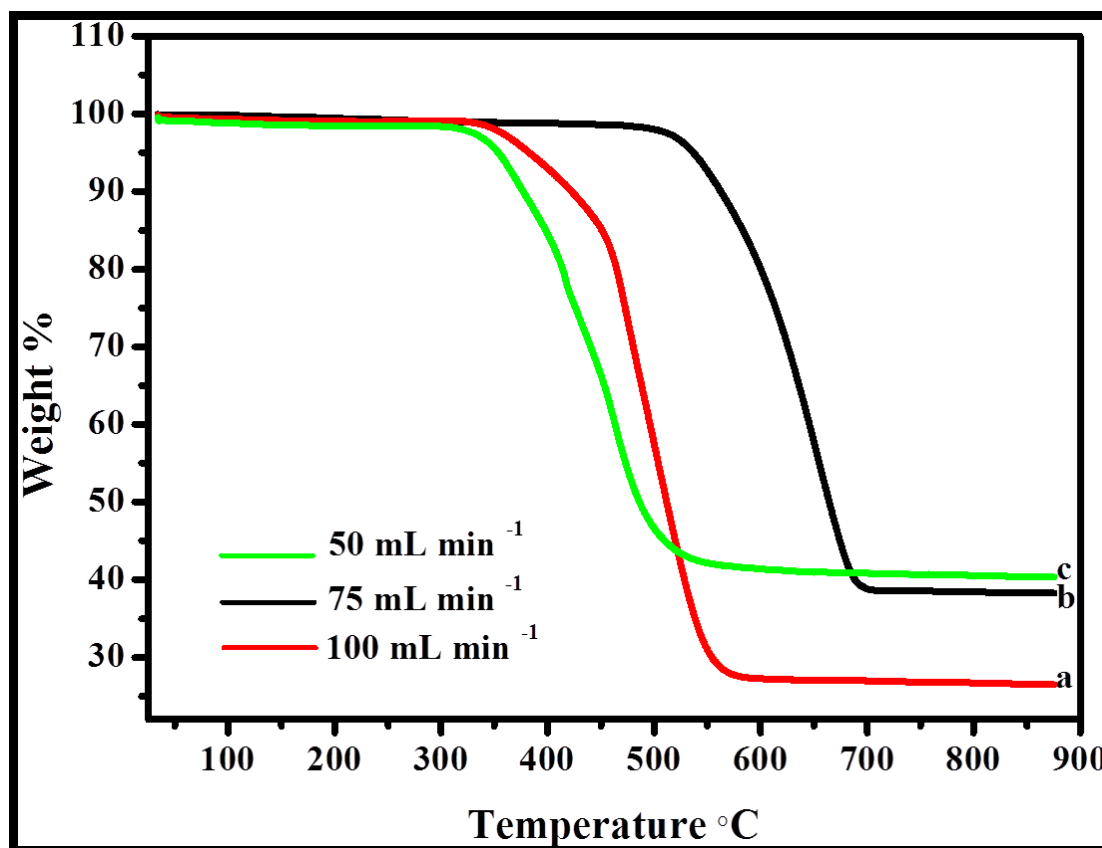


Figure 6.15 TGA of CNFs on 10 wt. % Ni/RANR for 1 h; 500 °C at (a) 100 mL min⁻¹ (b) 75 mL min⁻¹ and (c) 50 mL min⁻¹.

CNFs exhibit an important property in being more thermally stable to oxidation than activated carbon but more reactive than graphite.²⁶ The high residual weight of about 45 % in curve of **Fig. 6.15 (c)** implies that at 50 mL min⁻¹, there was lower carbon supply due to low concentration of C₂H₂ on the catalyst surface. The carbon materials formed were mostly amorphous disordered and short irregular fibers (**Fig 6.7 (a)**). At 75 mL min⁻¹ (**Fig. 6.15 (b)**), the CNFs shows that they are more stable than those synthesised at a lower flow rate of 50 mL min⁻¹ (**Fig. 6.15 (c)**) because even though their density coverage is lower, they are more crystalline and graphitic as shown in **Fig. 6.13 (b)** with a decomposition temperature of around 600 °C, an increase of more than 150 °C to that of CNFs synthesized at lower flow rate. **Fig. 16 (a)** shows a decomposition of up to about 75 % weight. This is because at this flow rate (100 mL min⁻¹), the coverage and density of the CNFs are very high such that the CNFs thermal decomposition took place at higher temperatures than the residual catalyst material.

6.4 Conclusions

The RANR morphology of the rutile support provided a unique topology on which Ni catalyst nanoparticles are sparsely dispersed in the smallest particle size possible (1 – 6 nm). Thus small particle size for the Ni particles was maintained even at higher metal wt. % loading. This serve control the thickness and coverage of the CNFs that can be synthesized over the Ni catalyst. The growth of fibers is consistent over a set of conditions required to achieve uniform coverage. Time variation has a direct effect on the degree of graphitisation in the CNFs prepared by CVD synthesis method. It can be concluded that the longer the time, the more graphitic are the CNFs. The D-band at all the respective time intervals seems to be of uniform intensity. This shows that the carbon crystallisation on the catalyst results in the formation of primary amorphous carbon. However the high metal wt. % loading and temperature do not increase the graphicity of the CNFs. The influence of temperature is to transform the carbon into graphitic material while the catalyst synthesizes and shapes the carbon material into its specific twisted morphology of the CNFs. Thus longer time exposure coupled with moderate to high temperatures, allows amorphous carbon material to crystallise into a more ordered graphitic form of the synthesized CNFs. The thermal stabilities of the CNFs can be tailored from the combination of the parameters of their synthesis conditions. TGA analyses proved that CNFs synthesized at 400 °C at a gas flow rate of 75 mL min⁻¹ over a widely dispersed catalyst distribution of 5 wt. % Ni/RANR will produce more crystalline, highly graphitic CNFs which are more thermally stable.

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Chapter 7

AuNPs supported on RANR for the synthesis of carbon nanomaterials

7.1 Introduction

For a long time gold was considered to be inferior to other noble metals as a catalyst.¹ This was because gold was difficult to deposit on metal oxides with dispersions as high as those of the other platinum group metals (PGMs), by using conventional methods such as impregnation.¹ However, co-precipitation and deposition-precipitation methods have provided useful alternatives for depositing AuNPs on supports to enhance their catalytic activity.² For example, recent studies have shown that deposition-precipitation was effective in the deposition of AuNPs with high dispersion on: MgO, TiO₂ and Al₂O₃.^{3–5} Here the choice of the metal oxide support was found to be crucial, as deposition of AuNPs on metal oxides with a point of zero charge below pH 5 was shown to be ineffective.⁶ In this regard TiO₂ has been widely studied as a support material because of its stability, ready availability, cheapness and ease of handling due to its amphoteric nature.⁷ This amphoteric nature of TiO₂ has allowed easy variation of the charge on the oxide surface by adjusting the solution pH below or above its point of zero charge.⁸ Hence this has implied that TiO₂ may serve as an ideal metal oxide support for AuNPs and consequently for use in the synthesis of SCNMs.

7.2 Literature Review

Gold has found a wide range of applications in recent years including for catalyst enhanced CVD (CECVD) synthesis of silicon nanowires (SiNWs) and CVD development of crystalline gallium nitride (GaN). Gold has also been used in catalysis to promote various reactions such as the decomposition of nitrogen oxides, water-gas shift⁹, CO removal, hydrochlorination, hydrogenation, liquid-phase selective oxidation, etc.¹⁰ The interest shown in using gold as a catalyst has been prompted by its propensity to exhibit high catalytic activity at low temperatures.^{11–13} In addition several studies have shown that when gold was stabilized, by being supported on metal oxides or activated carbon, it exhibited high catalytic activity.^{10,14} On the other hand, the use of gold in catalysis has also had some setbacks. For instance as a result of the use of chloride ions, the mobility of Au particles on supports has shown increased tendency to agglomerate, which is a severe limitation in catalysis.¹⁵

In this research titania was chosen to be a support for AuNPs, while DPU was chosen as the method of depositing the gold. In the former case, titania was chosen for a number of reasons. Firstly it was chosen because Au has been shown to ineffectively deposit on other oxide supports such as SiO₂ and WO₂.⁶ Secondly since titania has been determined to have a high point of zero charge ($PZC_{TiO_2} \sim 6$)¹⁶, this made it suitable for depositing Au at low pH values, while at the same time allowing high metal loadings to be attained. Thirdly titania, due to its high surface area, has been shown to be able to stabilize metal catalyst particles and hence enhance their catalytic performance.^{17–19} Lastly, unlike most of the titania that was used to support the above-mentioned metal catalyst particles, titania in the form of RANR was used in this study as it had unique long range order and topography where AuNPs could be deposited.¹⁷ In the latter case, DPU was chosen as a suitable technique for loading AuNPs onto these RANR supports, since work similar to that presented here showed that DPU was an efficient method for producing well dispersed AuNPs (< 8 nm) onto dandelion-like titania structures.²⁰ Hence this same technique was used extensively in the synthesis of the AuNPs/RANR catalysts that were used in this present study.

Gold has also been previously loaded on various types of supports including: metal oxides (e.g. α -Fe₂O₃, Mg(OH)₂ and TiO₂), CNTs (MWCNTs and SWCNTs) and CNFs, etc.^{21–23} AuNPs have even been used in the synthesis of CNTs by the CCVD process.^{24,25} Similarly, supported Au catalysts have been used to synthesise SWCNTs, MWCNTs and CNFs.^{26,27} Hence for all these reasons, the synthesis of AuNPs supported on RANR by the

DPU method is reported in this chapter. These AuNPs supported on RANR were then subjected to parametric studies (i.e. where temperature, time, flow-rate and catalyst wt. % composition were all varied) to investigate their ability to synthesise SCNMs via the CVD of acetylene under hydrogen (C_2H_2/H_2). Through characterisation (e.g. PXRD, TEM and SEM) of the AuNPs supported on RANR, as well as the carbonaceous products that were formed, the effects that these reaction parameters had on the morphology, crystallinity and graphitization of these products were then investigated. The results of these studies and are reported herein.

Previous studies report on the synthesis of single walled carbon nanotubes from Au nanoparticle catalysts. Au is a potentially interesting alternative to Fe, Co and Ni as a catalyst that is capable of catalysing SWCNTs growth. Bulk gold has historically been regarded as relatively inactive toward catalyzing chemical reactions due to its completely filled 5d shell and relative high first ionization energy.⁸ Over the past decade, however, it has been shown that nanoscale gold particles possess enhanced catalytic activity over their bulk counterpart due to size effects.^{4,9} Additionally, bulk Au has a melting point of 1064°C, and so, due to size effects, Au nanoparticles of diameters suitable for SWNT growth are expected to have melting points as low as 300 °C.¹⁰ This low melting point may enable lower CVD growth temperatures than is possible with Fe, Co, and Ni under otherwise identical conditions.²⁵ the growth of SWNTs using gold nanoparticle catalysts was successfully demonstrated by thermal CVD. Yoshikazu also reported on the synthesis of SWCNTs over Au nanoparticles. He concluded that Au nanoparticles smaller than 5 nm catalyse the synthesis of SWCNTs in a chemical vapour deposition. Au was also used to catalyse the synthesis of CNTs in a simple versatile in situ TEM method developed for investigating the nucleation and growth mechanism of the CNTs.²⁸ The quality of Au being able to be prepared in the smallest particle size (1-2 nm) was manipulated in previous research for the synthesis and diameter control of multi-walled CNTs over Au nanoparticle catalysts.²⁹

7.3 Experimental

7.3.1 Preparation of supported Au catalysts

In these studies the hydrothermal method of synthesis (as described in **Section 3.1.1**) was used to prepare RANR at 200 °C over 24 h. The AuNPs supported on RANR were synthesized using DPU. For this chloroauric acid hexahydrate ($\text{HAuCl}_4 \cdot 6\text{H}_2\text{O}$) was obtained from SA Precious Metals and titanium tetrachloride (TiCl_4) was obtained from Sigma Aldrich. DPU was carried out at 80 °C for 24 h (as described in **Section 3.1.3**) with subsequent washing and calcination at 700 °C. The DPU method enabled the loading of AuNPs of: 0.25, 1, 5, 8 and 10 wt. % to result in various Au/RANR catalysts that were then used for the synthesis of SCNMs.

7.3.2 Synthesis of CNFs

The set-up of the CVD process that was used in the synthesis of CNFs is found in **Fig. 3.1** (**Section 3.14**). As in previous cases, 500 mg of each of the Au/RANR catalysts was placed in a quartz boat that was positioned at the centre of the horizontal tube furnace. The temperature that was maintained at the centre of the furnace was varied from: 300 to 700 °C at 100 °C intervals. Acetylene gas (C_2H_2) was introduced into the tube reactor at a flow rate that varied from 50, 75 and 100 mL min^{-1} with hydrogen as the carrier gas set to the same flow rate as C_2H_2 . At all times, the temperature of the furnace was ramped up at a heating rate of 10 °C min^{-1} to the pre-set reaction temperature and was held at that temperature for a pre-set period of time. C_2H_2 and the carrier gas H_2 were both introduced via their respective inlet tubes at a uniform pre-set flow rate. After each reaction the furnace was allowed to cool down naturally to room temperature under the hydrogen gas which was allowed to flow throughout the duration of the reaction.

7.3.3 Characterisation of catalysts and carbon products.

The supported Au/RANR catalysts and the carbonaceous products that formed from the CVD reaction were treated in the same way as characterisations in **Section 6.3.3**. Furthermore, energy-probe microanalysis (EPMA) was used to determine the chemical composition of these carbonaceous products. Similarly, the catalyst surface areas as well as the spatial distribution of its components were mapped and profiled by EPMA through WDS.

7.4 Results and discussion

The supported Au/RANR catalysts and their carbonaceous products were characterised by a variety of techniques including: PXRD, EPMA, TEM, SEM, LRS and TGA. The results which were obtained are discussed in the sections which follow.

7.4.1 PXRD and EPMA analysis

The Au/RANR catalysts were initially characterised by PXRD and EPMA to determine their crystallographic nature as well as the spatial dispersion of their components. In the PXRD analyses, it was observed that the Au/RANR catalysts exhibited similar patterns throughout the whole range of deposition of the AuNPs on RANR (i.e. 0.25 – 10 wt. %), as seen by a representative diffractogram in **Fig. 7.1**.

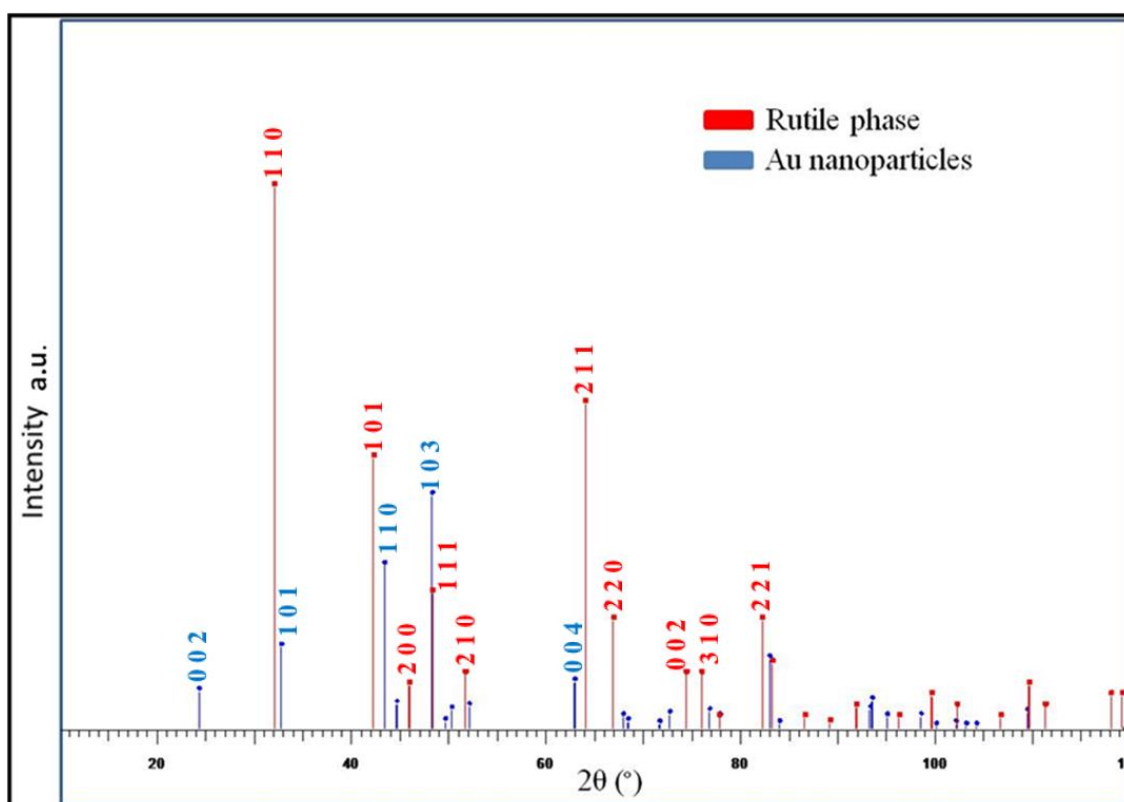


Figure 7.1: A representative PXRD diffractogram of a 5 wt. % Au/RANR catalyst.

The pattern in **Fig. 7.1** showed that RANR was composed of a pure rutile phase of titania, whose major peak occurred at 32° (2θ). In addition, typical lines of gold were observed whose major peak was located at 48.5° (2θ). This latter pattern conformed to that of ICSD Coll.Code: 58607³⁰ and revealed that the gold was in its zero oxidation state.³¹ This

observation was consistent with findings from Oros-Ruiz *et al.* who reported that gold supported on titania decomposed in air forming Au^0 because of the instability of Au_2O_3 .¹⁶

WDS profiles of the Au/RANR supported catalysts, a representative of which is seen in **Fig. 7.2**, were then obtained to complement the data obtained through PXRD.

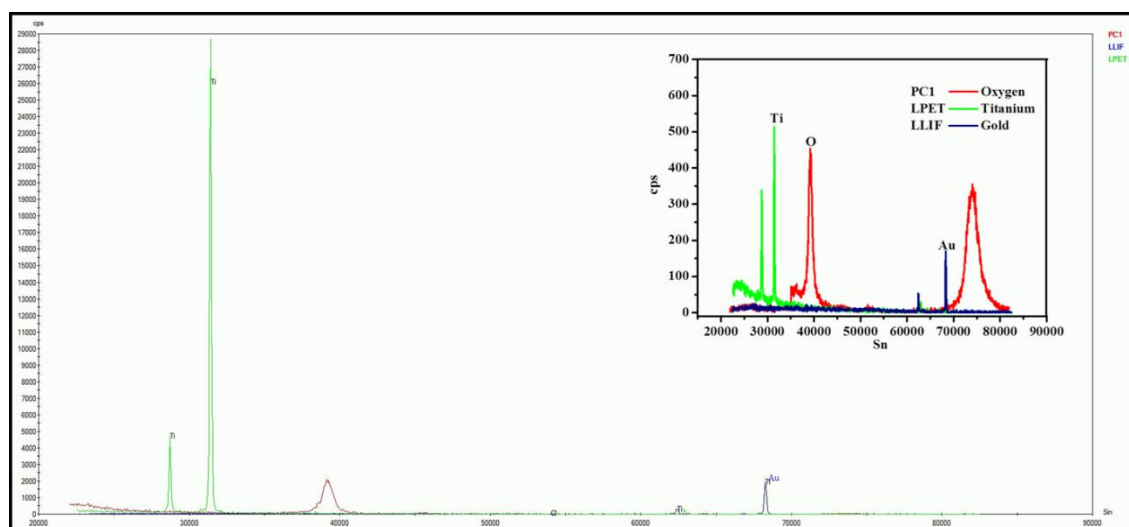


Figure 7.2: A WDS profile of 5 wt. % Au/RANR supported catalyst.

Using the wavelengths of the X-rays dispersed from the crystal lattice, these WDS profiles were utilised to determine the atomic counts in the Au/RANR catalysts. For example, in the WDS spectra of the 5 wt. % Au/RANR catalyst (**Fig. 7.2**), strong Ti and O peaks were observed at the lower signal points (Sn) of 32000 and 39000, respectively. However, at higher signal point values, the Au peak became substantively significant. Notably, the count per second (cps) of Au at this signal point was almost the same intensity as that of O at its lower signal point value. This implies that the density distribution of Au in the Au/RANR catalyst is almost the same as that of O. The insert in **Fig. 7.2** was a plot of the respective data points obtained by WDS, where two major peaks of the O-species at signal point values of 40000 and 75000 were observed. These peaks could most likely be due to oxygen in the RANR support. However, the possibility that this was residual oxygen associated with Au_2O_3 which gave rise to the AuNPs could not be ruled out. The Ti, O and Au in the Au/RANR were measured against the large pentaerythritol (LPET), pseudocrystal zero (PC0) and large lithium fluoride (LLIF) crystal standards respectively. As before, the peak intensity variation was comparable to the trend presented in PXRD pattern in **Fig. 7.1**. The heavier Au atoms had a peak intensity of 2500 cps, while Ti had a high intensity of 28800 cps and O about

5000 cps. This trend was also present in the EPMA maps of the Au/RANR catalysts as shown in **Figs. 7.3 (a)-(c)**.

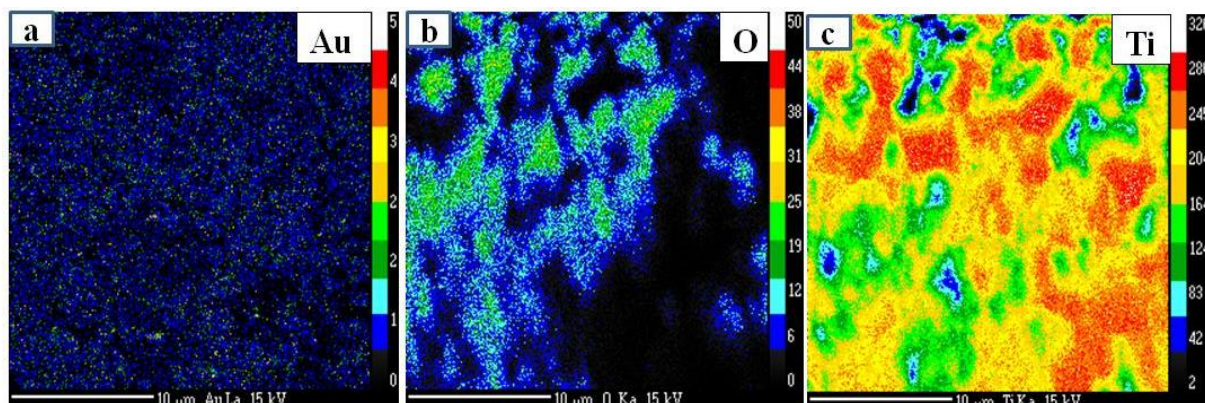


Figure 7.3: EPMA maps of a 5 wt. % Au/RANR catalyst showing the quantitative elemental compositions of: (a) Au, (b) O and (c) Ti.

The microscale elemental analyses shown in **Figs. 7.3 (a)-(c)** enabled qualitative data to be extracted about the identity and characteristics of the Au/RANR catalysts. For instance, although comparably low counts were obtained on the Au map (**Fig. 7.3 (a)**), this showed that the Au particles were similarly sized and homogeneously distributed on the support. On the other hand the high density of atomic counts of O and Ti (**Figs. 7.3 (b)** and **(c)** respectively), directly resembled the atomic distribution of the atoms in the rutile phase. Similarly, these EPMA maps represented the elemental concentration maps of the Au/RANR catalysts. For example, the bright rainbow colour on the Ti map (**Fig. 7.3 (c)**) showed that the support material was in higher abundance (i.e. had a higher concentration) as compared to the Au (**Fig. 7.3 (a)**). This was consistent with the how the catalyst was prepared i.e. 5 wt. % was Au while the other 95 wt% was the RANR support. For clarity, it must be pointed out that the reason why the AuNPs were observed at all on a micron scale, by the EPMA, was because these RANR supports had diameters in the range of 50 nm–3000 μm (as seen in **Fig. 7.5 (a)**).

7.4.2 Transmission and scanning electron microscopy

The morphologies of the Au/RANR catalysts were examined under TEM and SEM and the results can be seen in **Figs. 7.4 (a)** and **(b)** respectively.

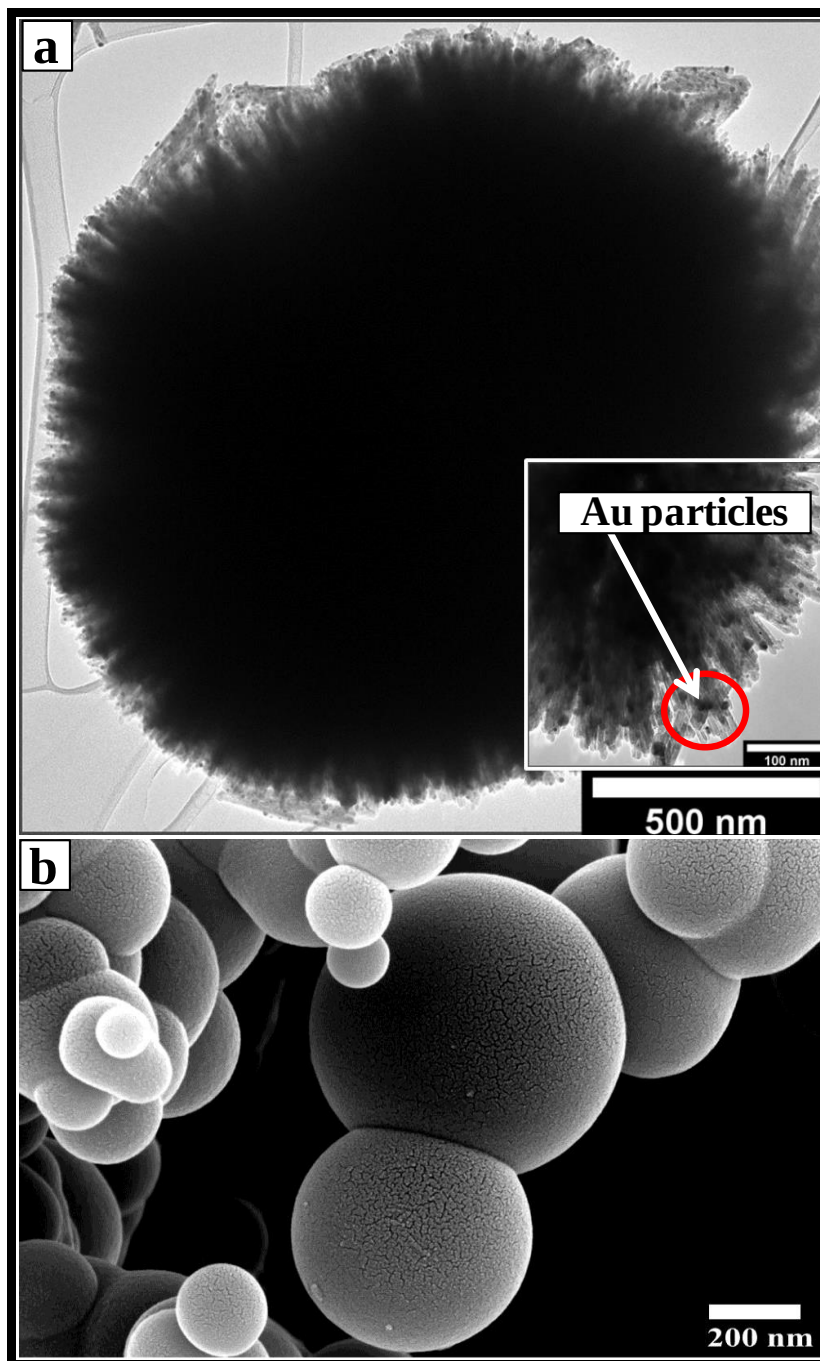


Figure 7.4: (a) TEM micrograph of a 5 wt. % Au/RANR catalyst. (b) SEM micrograph showing a 3D structure of the RANR.

Based upon these micrographs a number of observations were made. Firstly, that the RANR supports were spherical in structure and consisted of nanorods which were radially aligned (**Fig. 7.4 (a)**). However, PXRD analyses of these RANR supports had shown that they were composed of titania in the rutile phase (**Fig. 7.1**). Hence TEM (**Fig. 7.4 (a)**) had confirmed the presence of radially aligned rutile nanorods. Secondly, the surfaces of these rutile nanorods were observed upon closer examination (see encircled region in the enlarged area in **Fig. 7.4 (a)**) to be covered with darker coloured nanoparticles. Since PXRD as well as WDS had detected the presence of Au (**Figs. 7.1-7.2**), and EPMA had showed that Au was homogeneously dispersed on the support (**Fig. 7.3 (a)**), it was concluded that these darker coloured nanoparticles were AuNPs that had been deposited on these rutile nanorods by DPU. This was consistent with studies that have been conducted in our laboratory before, where it is believed that narrow spaces between these rutile nanorods controlled the sizes of the AuNPs that could be formed.³² Size distribution analyses of the rutile nanorods and the AuNPs were then conducted. The results are shown in **Figs 7.5 (a)-(b)**.

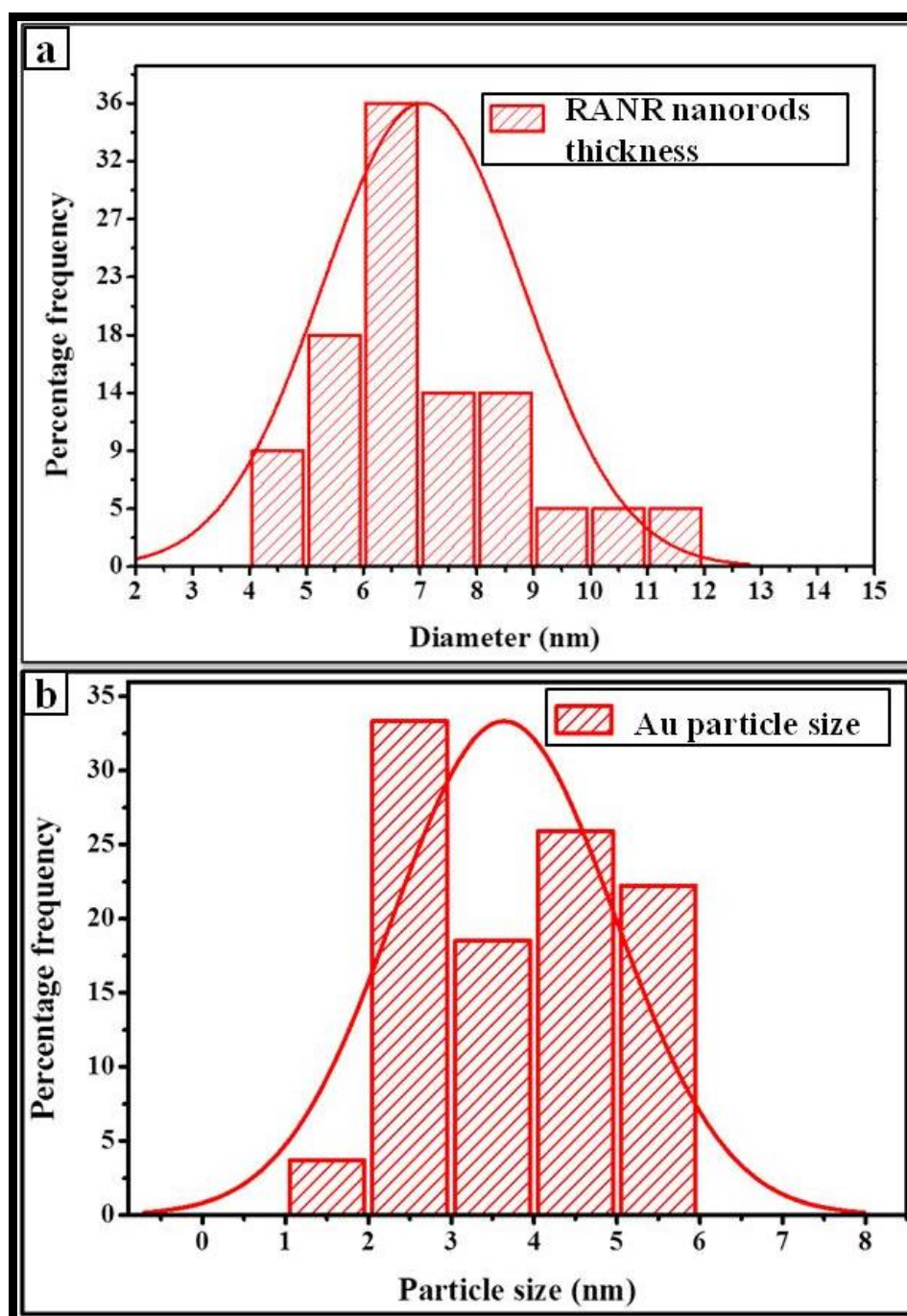


Figure 7.5: Size distribution analysis of (a) RANR nanorods diameter (b) Au catalyst nanoparticles supported on the RANR.

Here it was observed that the rutile nanorods had widths that ranged between 4–12 nm, and that the AuNPs ranged in size from 1–6 nm, as shown in **Figs. 7.5 (a) and (b)** respectively. It was therefore concluded that the RANR structure provided a unique topology on which these AuNPs were supported.

7.4.3 CVD synthesis of Au/RANR catalysed SCNMs

The Au/RANR catalysts were then tested for their ability to synthesize SCNMs in the CVD process that was previously described. Here it was found that the Au/RANR catalysts, at different wt. % loadings (i.e. 0.5, 1, 2, 5, 8 and 10 wt. %), catalysed the synthesis of a variety of SCNMs under different reaction conditions (e.g. temperature, time and flow rate). For example, the CVD products which formed over Au/RANR catalysts (0.5–2.0 wt.%) in 1 h, when the flow rate (75 mL min^{-1}) and temperature (i.e. 400°C) were kept constant, were observed to vary as can be seen in the TEM and SEM micrographs in **Fig. 7.6**. This is due to low Au particles distribution that the catalysts performed more like plain RANR which does not support synthesis of SCNMs.

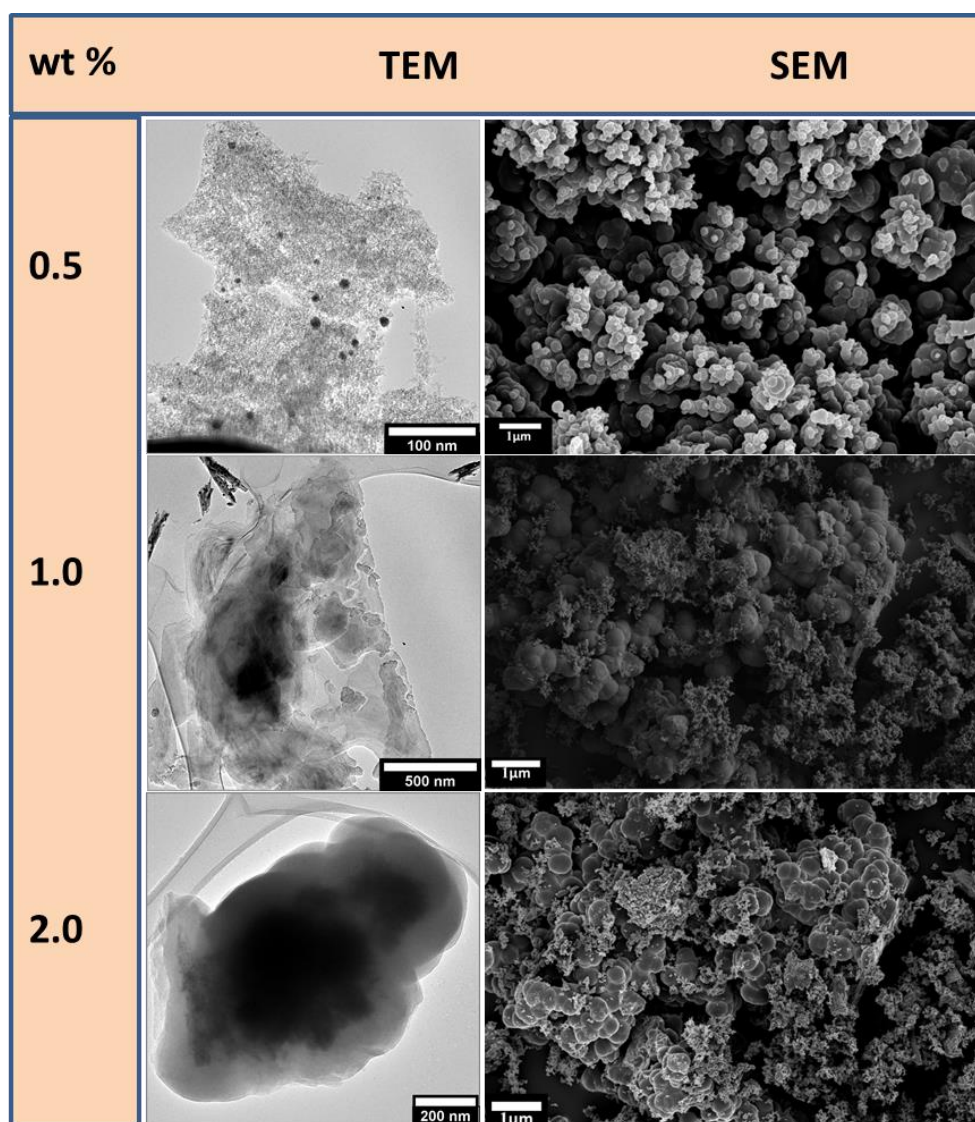


Figure 7.6: TEM and SEM analyses of the carbonaceous materials that were synthesized from Au/RANR catalysts (0.5, 1.0 and 2.0 wt. %) at 400°C , 1 h and 75 mL min^{-1} .

TEM and SEM micrographs in **Fig. 7.6** show that the low wt. % loading catalysts catalysed the formation of amorphous carbon material. The Au catalyst particles have crystal planes on which the carbon material is sufficiently shaped into structures such as SCNMs such as the observed CNFs. Detailed analyses of carbon nanomaterials synthesized over higher wt. % metal loading are presented in **Section 7.4.3**.

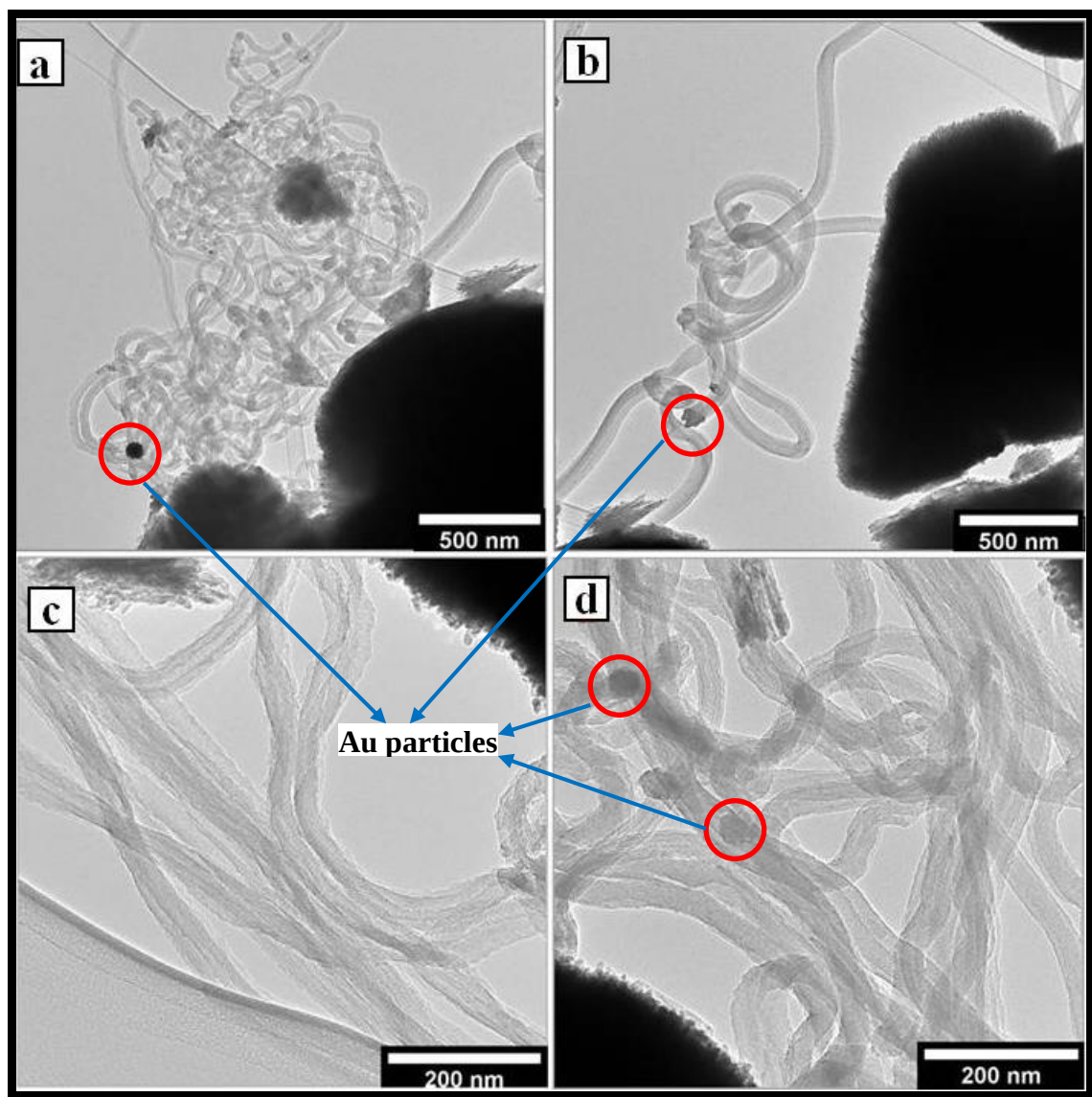


Figure 7.7: TEM micrographs of CVD-synthesized CNFs at: (a) 5 wt. % Au/RANR (b) 8 wt. % Au/RANR and (c and d) 10 wt. % Au/RANR at 700 °C for 2 h and a flow rate of 100 mL min⁻¹.

Au/RANR at higher wt. % loading was observed to catalyse the synthesis of both straight and coiled or twisted CNFs (**Figs. 7.7, 7.10** and **7.11**). **Section 5.4.2** presented detailed account of the growth mechanism of CNFs synthesised over La, a similar phenomenon observed for Ni (**Chapter 6**) and Au/RANR catalysts. Au particles were also observed on many of the tips of

the CNFs (see red circles in **Figs. 7.7** and **7.11**). This also implies that tip-growth occurred on RANR supported catalysts as the Au particles were dislodged from the RANR support. The CNFs were found to be characterised by different thickness and lengths attributable to the Au particle size on being dislodged from the support during CNFs growth. This phenomenon preceded temperature enhanced sintering and particles grew to larger sizes. The variations were brought about by variations in reaction parameters. Wt. % loading determined particle size of the Au catalyst to a large extent as it affected catalyst particles dispersion density. Increase in wt. % loading from 0.5 – 10 wt. % gave rise to increased dispersion density such that during sintering, more particles were available to form large sized particles. It is these sintered particles that determined the internal diameters of the CNFs synthesized. The gas flow rate and time period of catalyst-carbon source exposure had a direct effect on the CNFs' length and thickness (**Fig. 7.8**). However the supported Au catalysts favoured a tip-growth mechanism of synthesis as opposed to base-growth model. This phenomenon is exhibited by the fibers in **Fig. 7.7** micrographs which are characterized by Au catalyst particle at the tip of each fibre.

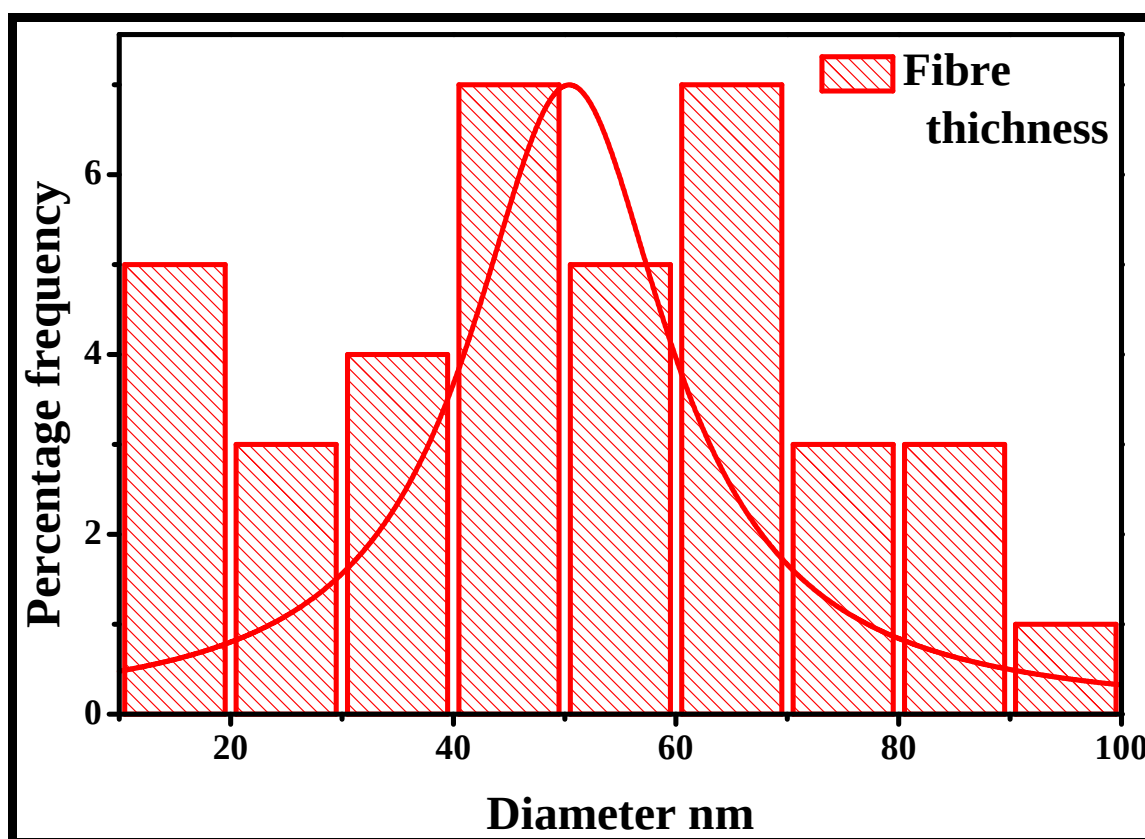


Figure 7.8: Fibre thickness distribution analysis of CNFs synthesized over 5 wt. % Au/RANR catalyst at 500 °C, 100 mL min⁻¹ for 2 h.

The fibers synthesized under different parametric conditions ranged from 10–100 nm in thickness with an average diameter of 50 nm. The wide range of thickness distribution was due to the polydispersion of the Au nanoparticle distribution and wt. % composition variation. It was determined that the tip-growth mechanism set the Au catalyst particle to serve as a seed around which the CNFs grew via a bottom – up mechanism.

7.4.4 Percentage weight loading

The catalyst material comprised AuNPs supported on RANR to give Au/RANR. wt. % Au loading ranged from 0.5–10 wt. %. This variation influenced and affected the particle distribution density and consequently the CNFs coverage. Under effective reaction parametric conditions, higher wt. % loading lead to higher CNFs deposition. It is apparent that at high temperatures (500–700 °C) and intermediate to high flow rates (75–100 mL min⁻¹), long, thick and more crystalline CNFs were synthesized. Catalyst wt. % loading is comparable to effect of concentration in the reaction system. It was observed that at low wt. % loading (< 5 %), none to very few CNFs formed for the whole range of parametric conditions (**Fig. 7.6**). Detailed studies showed that both the diameter and length distribution range increased drastically with increase in temperature.³³ This is because metal catalyst particles sintered or agglomerated to large sized particles that catalysed the synthesis of thicker CNFs. This was coupled by temperature enhanced decomposition of C₂H₂ and thus more carbon available for forming the carbon matrix of the CNFs. **Figs. 7.9 - 7.10** shows the effect of temperature variation with wt. % composition.

The properties and characteristics of the catalyst materials including large surface area, small Au particle size and high chemical stability at a wide temperature range, gives the catalysts good qualities and high catalytic activity and performance. **Fig 7.9** presents detailed analyses of CVD products synthesised over 5 wt. % Au/RANR at a C₂H₂/H₂ flow rate of 100 mL min⁻¹ over a 2 h period. TEM, SEM and LRS were used to show the effect of wt. % with temperature.

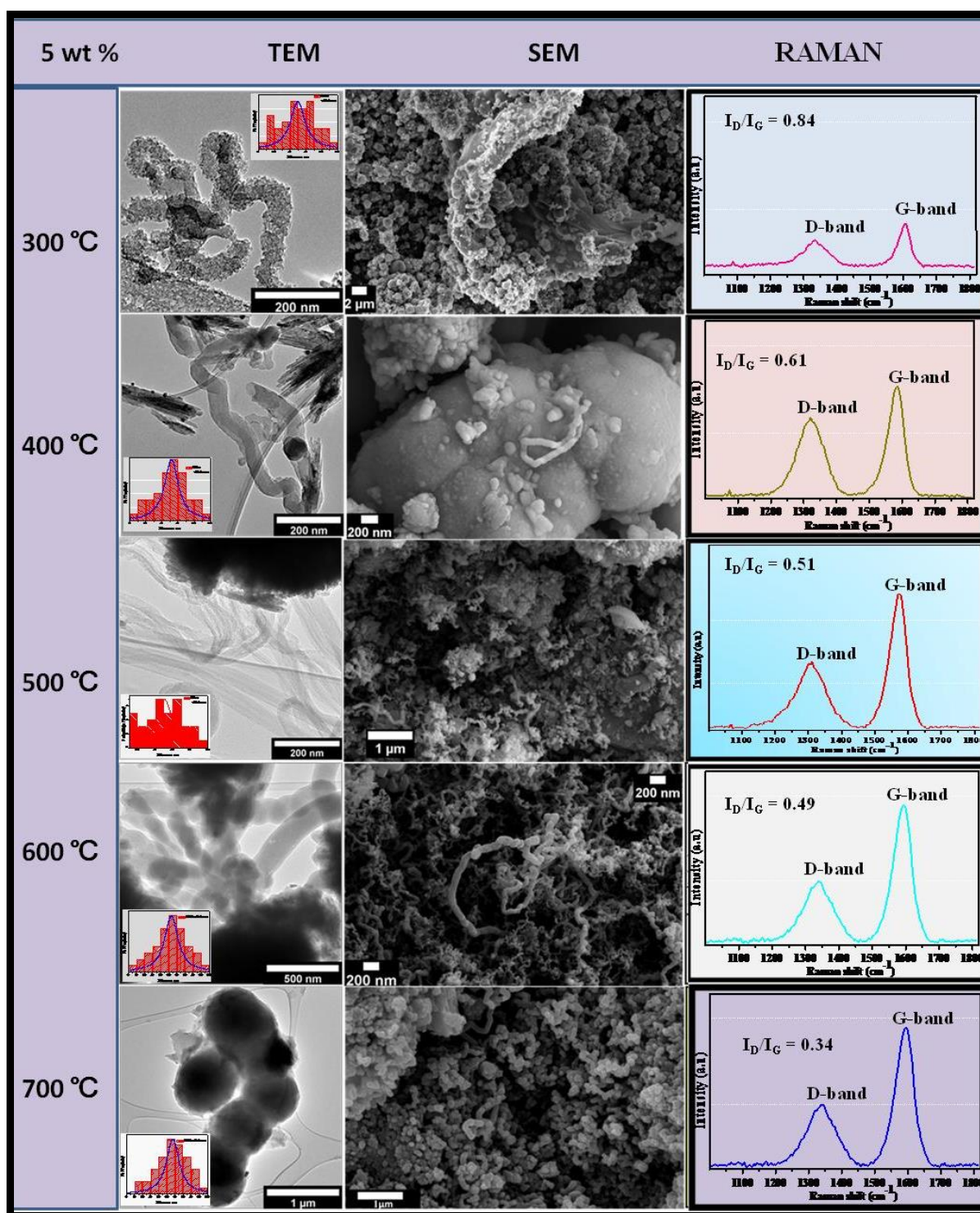


Figure 7.9: TEM and SEM Comparisons of carbon nanomaterials synthesized at different temperatures over 5 wt. % Au/RANR, 2 h, 100 mL min⁻¹.

At 5 wt. % Au composition, it was observed that CNFs coverage, crystallinity and graphicity increased with temperature. The fibers synthesized over the 5 wt. % catalyst are simple straight chain fibers having a diameter range of 10 – 100 nm (**Fig. 7.9**). The average CNFs diameter was observed to increase with an increase in temperature from 50 nm to 58 nm over the 300 – 700 °C range (CNFs thickness distribution analyses inserts on TEM micrographs in **Fig. 7.9**). Raman spectra showed how the G–peak became more intense than the D–peak with increase in temperature. **Fig 7.9** showed I_D/I_G ratios decreasing with increase in temperature from 0.84 at 300 °C to 0.34 at 700 °C. It may be concluded that at 5 wt. %, the Au/RANR catalyst supported growth of graphitic CNFs at high temperatures with an average diameter that also increased with temperature. This phenomenon was also observed on CNFs synthesized over 5 wt. % Au/RANR at 30 min and 1 h time intervals (**Appendix C**). This implies that both wt. % and temperature influenced the degree of graphicity of the CNFs synthesised in the CVD reactions. **Table 7.1** summarises the trends of the characteristics of the CNFs synthesised over 5 wt. % Au/RANR at 100 mL min⁻¹ over a 2h period.

Table 7.1 Trends in characteristics of CNFs synthesized over 5 wt. %, 100 mL min⁻¹, 2 h

T °C	300	400	500	600	700
CNFs Mean Dia. (nm)	50	52	52	55	58
I_D/I_G	0.84	0.61	0.51	0.49	0.34
TGA T °C	380	350	420	580	580

Table 7.1 also presented the thermal decomposition temperatures of the CNFs synthesised under these parametric conditions. It was observed that the decomposition temperature shifted towards higher values with increase in temperature. This is attributable to increased graphicity and crystallinity of the CNFs as shown by the increase in I_D/I_G ratios with temperature.

Increased CNFs density was observed at 8 wt. % Au/RANR. However, at 600 °C, the CNFs produced had a perfect coiled morphology as shown in TEM and SEM micrographs in **Fig. 7.10**. A mixture of coiled and straight CNFs was produced at 700 °C. This implied that at high temperatures, there is rapid C₂H₂ decomposition and nucleation of carbon such that shaping of the fibers into perfect coils was inconsistent. Detailed analyses revealed that at 8 wt. %, the mean diameter (inserts on TEM micrographs in **Fig. 7.10**) of CNFs synthesised

across the 300 to 700 °C temperature range was higher as compared to those of CNFs synthesised over 5 wt. % Au/RANR. The CNFs mean diameter increased from 76 nm at 300 °C to 85 nm at 700 °C (see **Table 7.2**). Similarly, LRS analysis showed increase in graphicity with temperature.

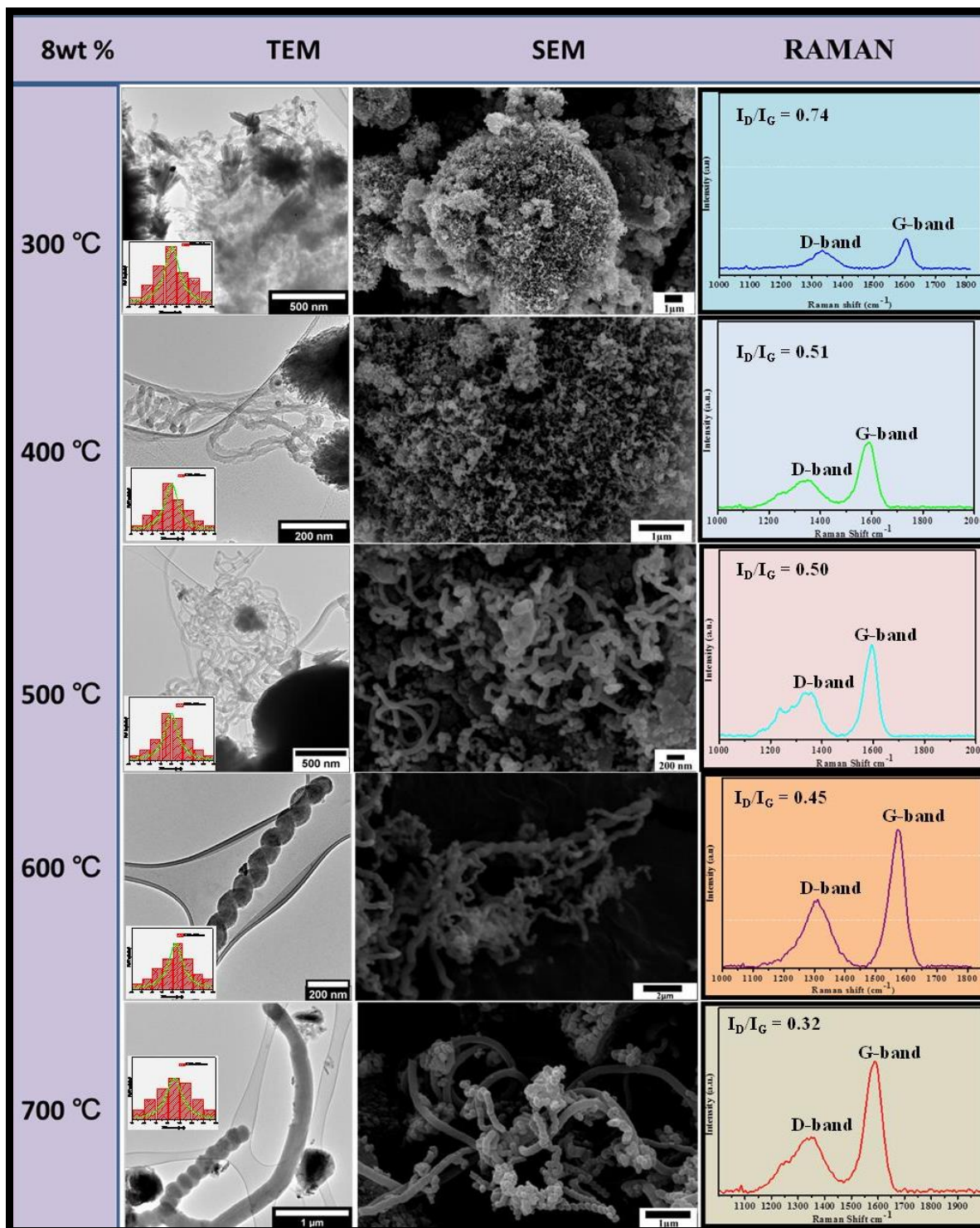


Figure 7.10: TEM and SEM Comparisons of carbon nanomaterials synthesized at different temperatures over 8 wt. % Au/RANR 2 h, 100 mL min⁻¹.

I_D/I_G ratios of CNFs synthesised over 8 wt. % Au/RANR presented in **Fig. 10** decreased with increase in temperature. It was also observed that these ratios are lower than those of CNFs synthesised over 5 wt. % Au/RANR. I_D/I_G ratios of CNFs on 8 wt. % Au/RANR decreased from 0.74 at 300 °C to 0.32 at 700 °C. This implied that the 8 wt. % Au/RANR synthesised more crystalline and graphitic CNFs than those over 5 wt. % Au/RANR. However, TGA analysis showed similar decomposition temperatures of CNFs over both 5 and 8 wt. %. This can be explained in terms of the same respective temperatures over which they were synthesized. **Table 7.2** compares trends in the characteristics of the CNFs synthesised over 8 wt. % Au/RANR.

Table 7.2 Trends in characteristics of CNFs synthesized over 8 wt. %, 100 mL min⁻¹, and 2 h.

T °C	300	400	500	600	700
CNFs Mean Dia. (nm)	76	78	80	83	85
I_D/I_G	0.74	0.51	0.50	0.45	0.32
TGA T °C	380	350	420	580	580

The data presented in **Table 7.2** showed that at 8 wt. %, both CNFs mean diameter and decomposition temperature increased with an increase in temperature. This corresponded to the observed decrease in I_D/I_G ratios. It can be concluded that at 8 wt. %, the catalyst supported the synthesis of more graphitic CNFs. The observed improved characteristics are attributable to coiling that suggests increased crystallinity in the carbon framework of the fibers.

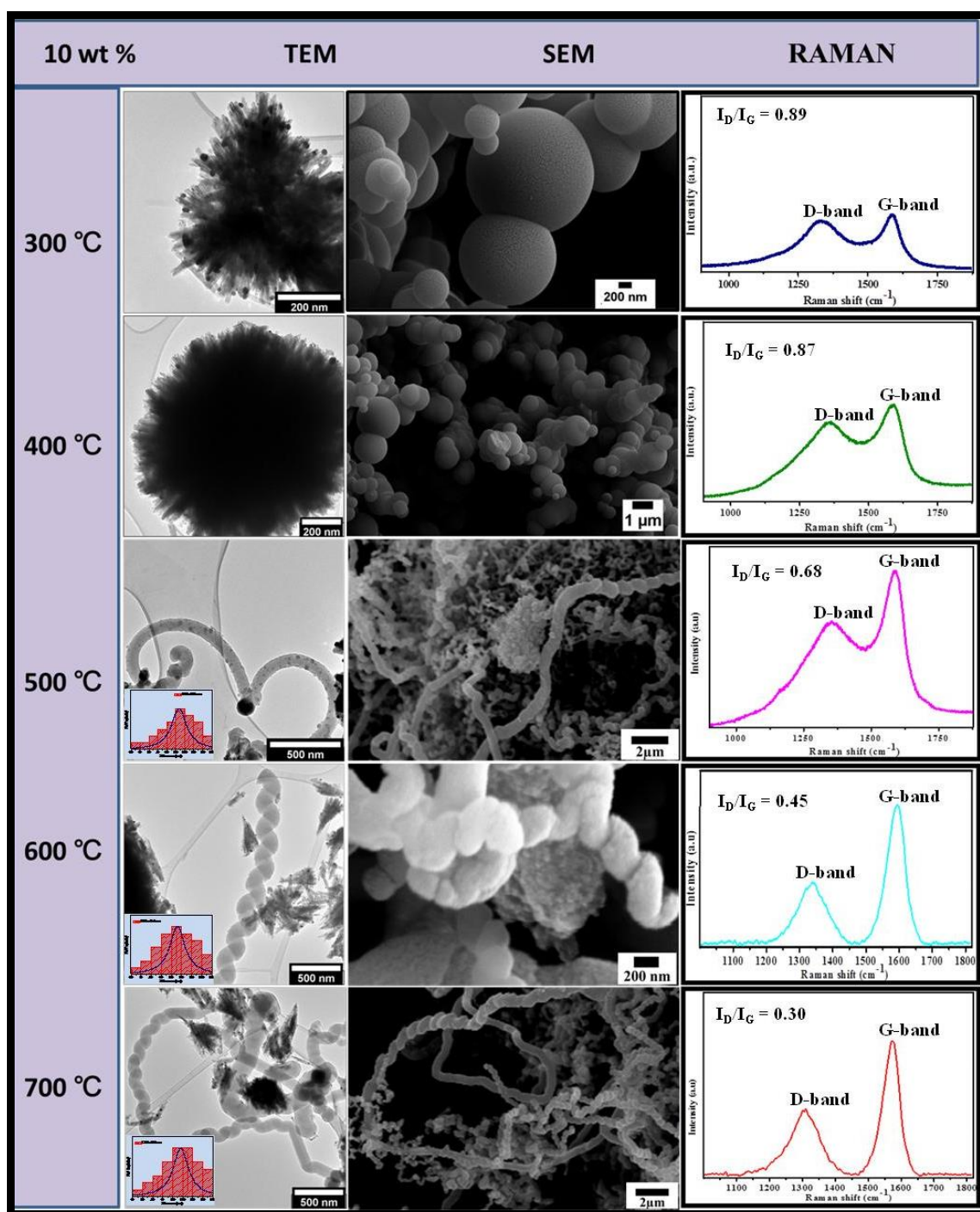


Figure 7.11: TEM and SEM Comparisons of carbon nanomaterials synthesized at different temperatures over 10 wt. % Au/RANR 2 h, 100 mL min⁻¹.

Similar trends were observed with 10 wt. % Au/RANR catalysts. However, at low temperatures (300–400 °C) the C₂H₂ did not decompose to make C available for the synthesis of CNFs compared to what was observed at higher temperatures (500–700 °C). This phenomenon did not change even at a consequential increased metal loading of 10 wt. % as

shown in TEM and SEM micrographs in **Fig. 7.11**. As a result of the low reaction temperatures, very little carbon materials were synthesized which were mostly amorphous as shown by their respective Raman spectra. TEM and SEM micrographs in **Fig. 7.11** are showing catalysts with no carbon materials of any morphology at 300 – 400 °C. High I_D/I_G ratios were observed at these temperatures suggesting that highly amorphous carbon accumulated on the catalysts. At 500 – 700 °C, CNFs of predominantly coiled or twisted morphology were synthesized and a few straight chain CNFs were produced as shown in the TEM and SEM micrographs in **Fig. 7.11**.

Detailed analysis showed that the CNFs increased in diameter ranges with increase in temperature. The I_D/I_G ratios sharply decreased at this temperature range from 0.68 to 0.30 (**Table 7.3**), showing that the mostly coiled CNFs were of high graphicity and crystallinity. **Table 7.3** compares the trends in the characteristics of CNFs produced during CVD using 10 wt. % Au/RANR.

Table 7.3 Trends in characteristics of CNFs synthesised on 10 wt. %, 100 mL min⁻¹, and 2 h

T °C	300	400	500	600	700
CNFs Mean Dia. (nm)			104	106	108
I_D/I_G	0.89	0.87	0.68	0.45	0.30
TGA T °C	320	340	420	580	600

Compared to trends presented in **Tables 7.1** and **7.2** for CNFs syntheses at 5 and 8 wt. % respectively, **Table 7.3** presented trends that are at higher ranges of reaction conditions. The CNFs mean diameter at 104 – 108 nm for 500 °C < T °C < 700 °C, I_D/I_G ratio at 0.89 – 0.30, and a decomposition temperature range of 320 – 600 °C. This implied that the high wt. % gave rise to Au particles of largest particle sizes that catalysed the synthesis of CNFs with the highest diameters, with largest degree of crystallinity and graphicity. However, CNFs density around was lower mainly because sintering could have taken place to a large extent that most Au particles lost their catalytic activity. The effect of flow rate and time variation was studied in details in the following section.

7.4.5 Gas flow rates and time variation

In this work, the gas flow rate was varied from 50–100 mL min⁻¹ while all other parameters were alternatively held constant. The flow rate of the gas mixture determined the overall vapour pressure in the reaction region of the CVD setup. The influx of C₂H₂/H₂ to the catalysts bed in the quartz boat and its catalytic decomposition is a function of the flow rate and time of exposure of the catalyst to the carbon source. Detailed analysis showed that low flow rates and short time periods yielded no to very little CNFs (**Fig. 7.12(a)**). Whereas intermediate to high flow rates favour more crystalline, more graphitized and densely covering CNFs (**Fig. 7.12(b)**). High flow rates are at times characterised by highly disordered CNFs and amorphous carbon materials (**Fig. 7.12(c)**). This is because at low flow rates (< 50 mL min⁻¹), and short time (30 min), the catalysts receive too little carbon that can be synthesized into CNFs. At longer periods (1–2 h), the little carbon received is used to make short but highly graphitized CNFs. The intermediate flow rate (75 mL min⁻¹), allows sufficient interaction of the carbon and the catalyst such that proper knitting of the CNFs matrix takes place consistently. However a combination of high flow rate and high temperature only supports the synthesis of pyrolysis products with a few CNFs. The lack of more ordered well-knit carbon materials is because of the high flow rates that result in rapid accumulation of carbon and clogging the catalysts such that less crystallisation takes place as shown in **Figs. 10 - 12**. At high temperatures, the rapidly accumulating carbon is converted to pyrolytic products such as glassy carbon and carbon nanospheres.

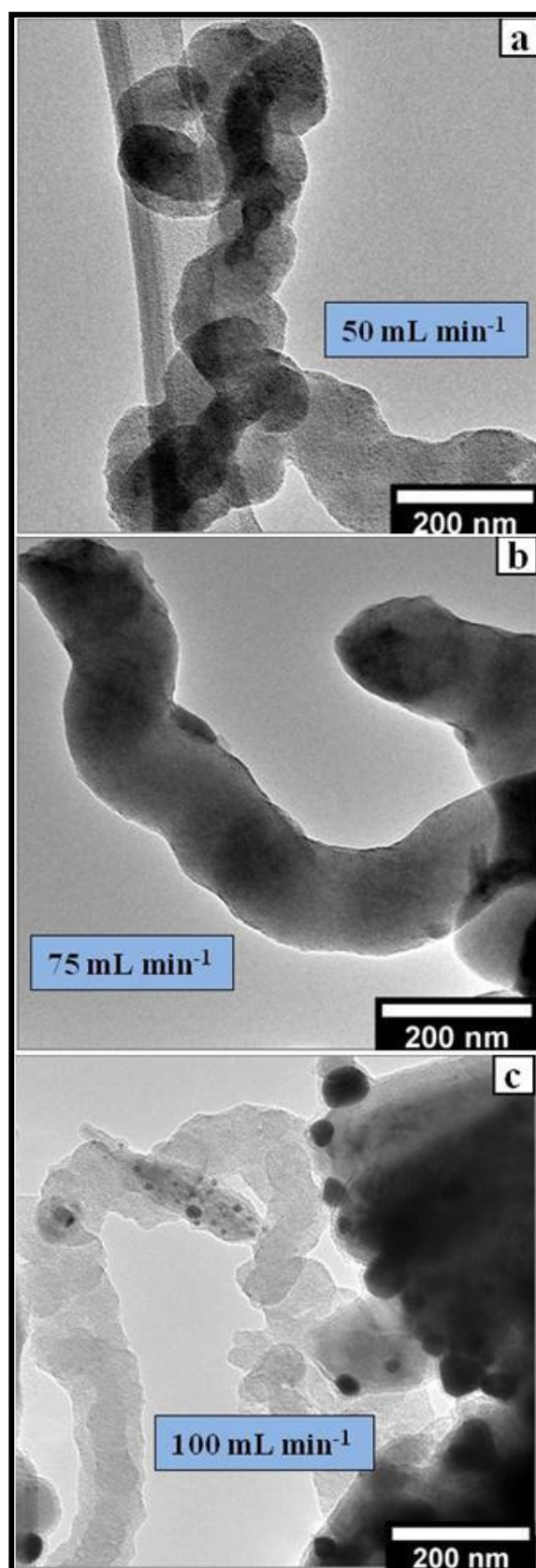


Figure 7.12: TEM micrographs of CNFs synthesized at different flow rates at (a) 50 mL min⁻¹, (b) 75 mL min⁻¹ and (c) 100 mL min⁻¹ over 8 wt. % Au/RANR 2 h, at 500 °C.

7.4.6 LRS

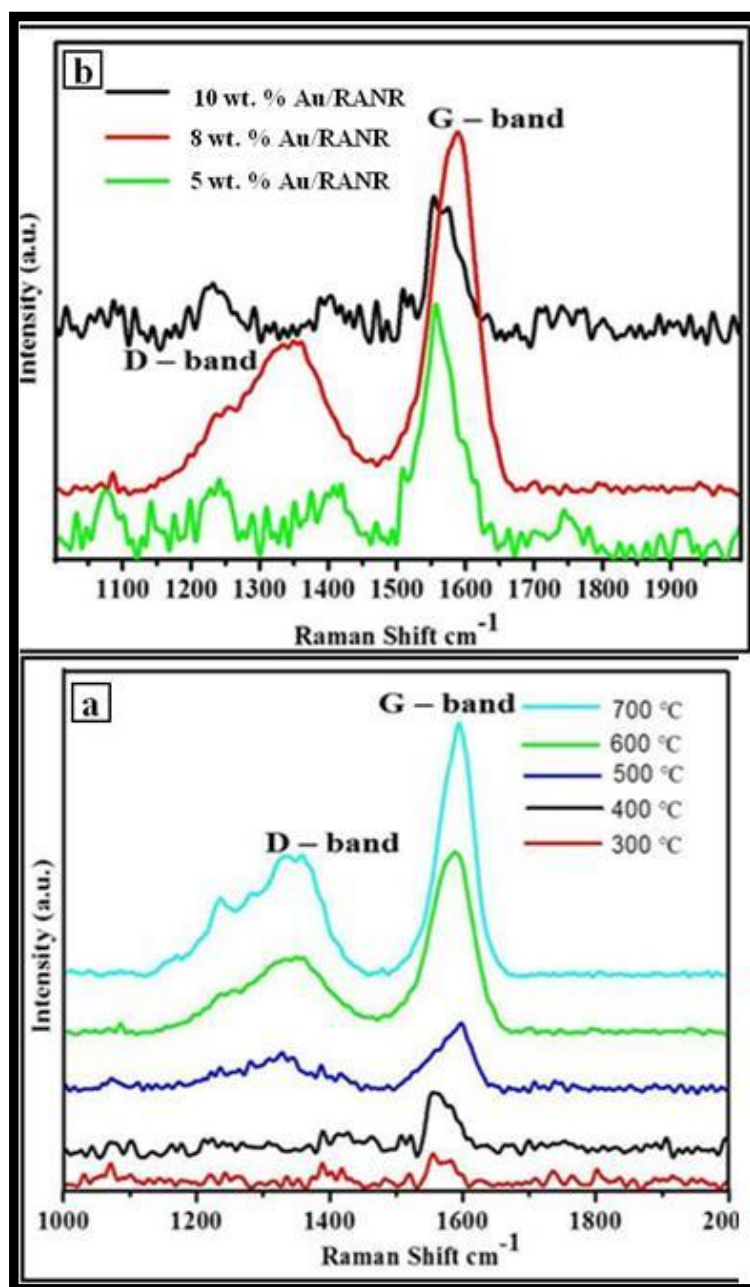


Figure 7.13: Laser Raman spectra of CNFs (a) Synthesis over 5wt. % Au/RANR catalysts at different temperatures, (b) CNFs synthesized on catalysts at different wt. % loading under uniform conditions (1 h, 100 mL min⁻¹, 500 °C).

Laser Raman spectroscopic measurements performed on the CNFs synthesized over the supported Au/RANR catalysts showed D and G-band peaks of selected CVD products. In **Fig. 13(a)**, the G-band shifted more towards 1600 cm^{-1} with an increase in temperature. This is due to tangential modes corresponding to vibrations of the C–C bonds in the plane of

graphitic carbon matrix of the CNFs which became stronger with increase in temperature.³⁴ This implies that high temperatures (500–700 °C) propagate temperature-enhanced decomposition of the C₂H₂ making carbon sufficiently available for the synthesis of more ordered form of the CNFs (**Figs. 7.10** and **7.11**). It was observed that the higher the reaction temperature, the more intense the G-band peak. This is because crystallinity of the CNFs increased with an increase in temperature as the orderliness result in more sp² hybrid bonding in the carbon and hence more graphitisation. The Raman spectra in **Fig. 7.12(a)** show that the G-band occurring around 1590 cm⁻¹ is more intense than the D-band occurring around 1350 cm⁻¹. Their intensities generally increased with temperature.³⁵

It was expected that graphitization will generally increase with wt. % loading due to increased catalytic effect. **Fig. 7.12 (b)** shows that the trend is not as expected. This is because at lower wt. % loading, the density of catalyst coverage is very low and thus there is increased catalytic conversion of carbon to fibrous carbon material. However, there is significant graphitisation from a combination of other reaction parameters such as time and temperature as shown by the Raman spectrum for CNFs on 5 wt. % Au/RANR in **Figs. 7.9 and 7. 12(b)**. At 8 wt. % loading, there is sufficient catalyst on the reaction interface such that efficient conversion takes place and CNFs that are more graphitic are produced. At 10 wt. % loading the G-band peak seems to be lower. This coupled with other reaction parameters suggest that a lot of carbon is dissolved into the catalyst and atomised (**Fig. 7.12(c)**). However the high influx of carbon favours accumulation of amorphous carbon while little carbon is sufficiently crystallised into a more graphitised form in the CNFs formed. It can be inferred that wt. % cannot be distinctively used to account for the Raman performance of the carbon nanomaterials synthesized over catalysts of different loadings.

7.4.7 Thermogravimetric analysis (TGA)

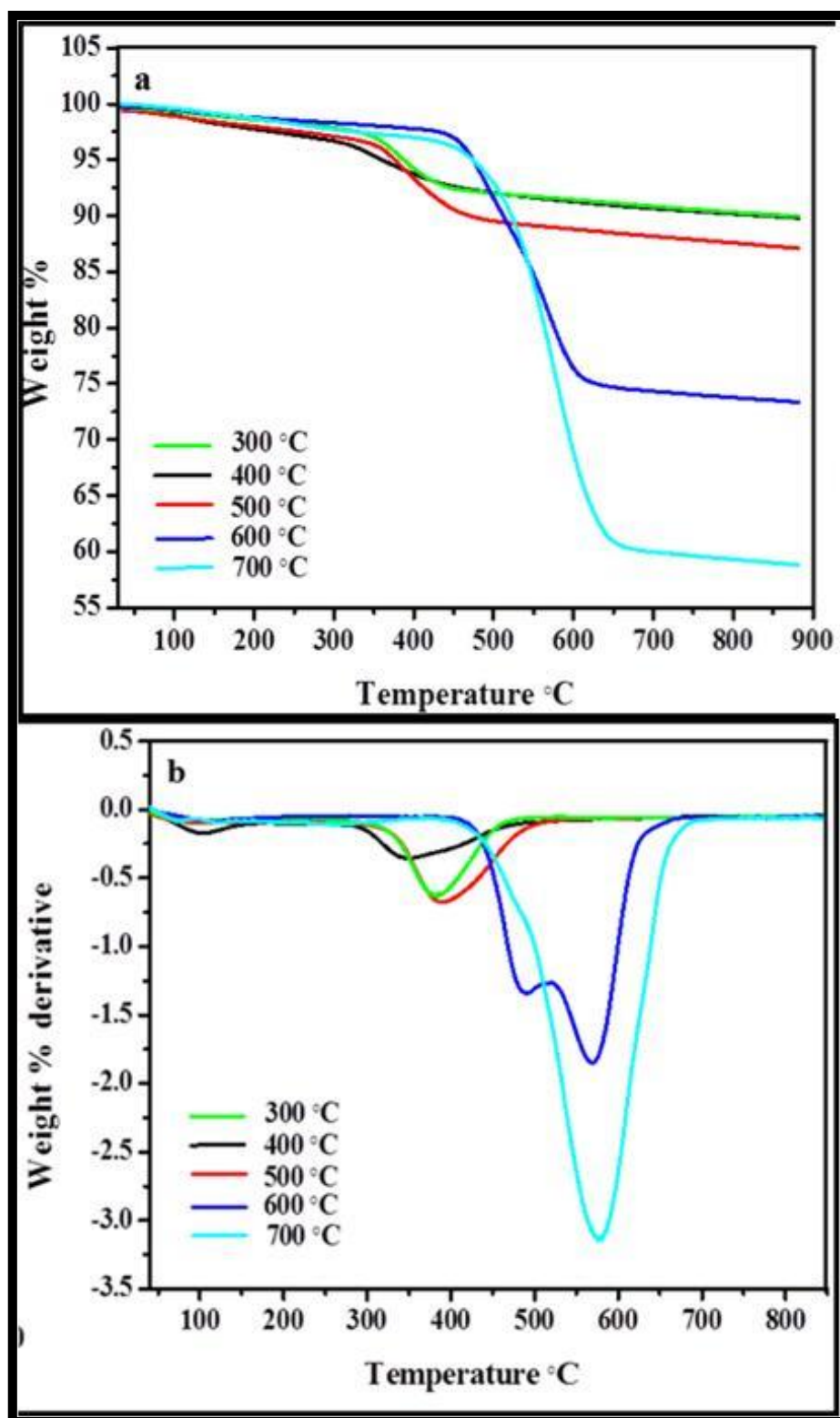


Figure 7.14: TGA profiles of CNFs (a) Synthesis over 5 wt. % Au/RANR catalysts at different temperatures, (b) The derivative plot of the wt. % against temperature of the CNFs in this TGA analysis (uniform conditions: 2 h, 100 mL min⁻¹).

Temperature has exhibited great influence on the nature of the CNFs synthesized under different conditions. Thermogravimetric analysis of CNFs synthesized over 5 wt. % Au/RANR confirmed a trend presented in Raman analysis. **Fig. 7.14(a)** is a TGA profile of CNFs synthesized over a period of 2 h and gas flow rate of 100 mL min⁻¹. The temperature variation presented in **Fig. 7.14** suggests that the CNFs became more thermally stable with an increase in temperature. At low temperatures very little CNFs formed and were mostly amorphous and where graphitisation occurred, the yield was very little. Hence less than 10 % of material decomposed at a temperature range 300–500 °C and the 90 % residual weight comprises mainly the catalyst material which is thermally stable.

Fig. 7.14(b) shows that for CNFs synthesized at 600 °C there are two decomposition temperatures at 500 and 600 °C. Decomposition at 500 °C may be attributed to amorphous and the less crystalline carbon in the CNFs while that at 600 °C is due to the more crystalline graphitized carbon form of the CNFs. The more ordered the carbon network in the CNF matrix, the more thermally stable the carbon material as a result of strong bonding in the sp² hybrid bonding in the carbon framework of the CNFs. **Fig 7.14(a)** and **(b)** shows that the crystallinity of the as-synthesized CNFs produced at 700 °C is high. The weight loss at this temperature is also increased (60%) indicating high purity and more graphitised CNFs. This indicates that high temperatures result in the Au/RANR possessing the highest selectivity towards the growth of more crystalline and highly graphitised CNFs.

7.5 Conclusions

The RANR morphology provided a unique topology on which AuNPs were deposited with homogeneous dispersion. The ability of DPU method to afford monodispersion of the AuNPs along the radial length of the nanorods of the RANR enabled Au to be deposited in very small particle size range with average diameters of around 4 nm. EPMA elemental analysis confirmed the spatial distribution of the AuNPs in the Au/RANR catalysts matrix. Depositions ranging from 0.5–10 wt. % were achieved. It can be concluded that the wt. % composition can be used to control particle size distribution of the AuNPs, while the particle size determine the thickness of the CNFs synthesized where particles may be held in fixed positions on the RANR support. It was also observed that the mechanism of CNFs growth may be described as the tip-growth method as the CNFs are characterised by an Au–seed at the tips of the fibers. The RANR morphology as presented on TEM micrographs, did not hold the AuNPs in fixed positions allowing sintering and agglomeration of AuNPs. This resulted in further loss of control of the CNFs thickness. The CNFs synthesized had larger diameters (10 – 100 nm) than that could be suggested by the particle size of the supported Au nanoparticles (1 – 6 nm). The parametric reaction conditions have a synergic effect on the overall characteristics of the CNFs synthesized. Thus temperatures significantly contribute towards the formation of ordered forms of CNFs hence their degree of graphicity.

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Chapter 8

Chemical vapour deposition synthesis of carbon nanomaterials over lanthanum-nickel mixed-metal catalyst supported on novel RANR

8.1 Introduction

The performance of metals used as catalysts varies greatly over a wide range of parameters such as their particle size, the reaction medium, temperature and support materials they are loaded on. A suitable method of metal loading has to be determined considering factors such as pH, point of zero charge, particle size and stability.¹ Titanium dioxide has been used in both its anatase and rutile phases as a metal nanoparticle support to produce catalyst materials.²⁻⁷ RANR were used as an alternative support material in the preparation of La-Ni/RANR co-loaded metal catalyst for the synthesis of shaped carbon nanomaterials (SCNMs). This was of interest to see if the inclusion of two metals would produce synergistic effect. Many methods for loading metal nanoparticles are available for the preparation of this catalyst. La and Ni nanoparticles were loaded on RANR to give La-Ni/RANR co-loaded catalysts using a hydrothermal method and deposition-precipitation with urea (DPU).^{8,9} The La-Ni/RANR co-loaded catalysts were explored for the synthesis of carbon nanofibers (CNFs) via a chemical vapour deposition (CVD) method. Previous analyses (see **Chapter 4**) using PXRD revealed occurrence of oxide phases of La, Ni and the bimetallic La-Ni in the crystallographic phases La_2O_3 , NiO , LaNiO_3 and La_2NiO_4 respectively.¹⁰ The reduction of the loaded metal oxides produced small sized La-Ni nanoparticles. The small particle size range promoted high catalytic activity. Ni has a tendency of synthesising coiled CNTs or twisted CNFs while La however, has a tendency of synthesising straight CNFs. PXRD; EPMA and TPR analyses were useful techniques in determining the intrinsic properties and characteristics of the supported co-loaded catalysts. TEM, SEM, Raman and TGA characterisations allowed detailed morphological studies of both the La-Ni/RANR catalysts and the carbon nanomaterials synthesized.

8.2 Literature Review

Titania exists in three main polymorphs, namely anatase, brookite and the more thermodynamically stable rutile phase.¹¹ Anatase TiO_2 has been used to support nanosized particles of different materials to produce different catalyst materials. Mono-, bi- and polymetallic types of catalysts have been previously prepared using TiO_2 via different methods such as sol-gel, conventional impregnation, colloidal, Pechini, self-combustion, wet impregnation and facile hydrothermal methods.^{2, 3} Many previous works involving mono and heterogeneous catalysts were faced with various degrees of catalyst sintering and agglomeration. For example, supported gold is catalytically active when it is dispersed as small particles on an oxide support for CO oxidation. However deactivation sets in due to nanoparticles sintering and formation of carbonates on the reactive sites. This phenomenon was postulated to be surmountable by preparing co-loaded catalysts.⁸

Supported co-loaded catalysts have proved to exhibit significant improved catalytic activity, enhanced stability and synergetic effects both in their chemistry and performance.¹⁴ Co-loaded metal nanoparticles in a catalyst have a capacity of inducing geometric modifications of the respective metal surfaces rendering the catalysts more efficient. La-Ni co-loaded catalysts have previously been prepared on different supports such as alumina and silica. Ni/ Al_2O_3 has been prepared for use in steam reforming of ethanol and phenol.^{15,16} However, adding La to form La-Ni/ Al_2O_3 catalyst stabilised the alumina support and improved the resistance to coking of the Ni/ Al_2O_3 in various steam reforming reactions.¹³

Zhang et al. studied the catalytic performance of Ni-based catalysts using the support of $\gamma\text{-Al}_2\text{O}_3\cdot\text{SiO}_2$ and investigated the effect of the second metal of La, Y, Co, Cu and Zr on catalytic performance of Ni/ $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ catalysts.¹⁷ It was indicated that low amount of La additives (5%) was enough to inhibit Ni crystal growth and enhance the reduction of nickel oxide. However, Garbarino and co-workers carried out a study on Ni/ Al_2O_3 and Ni-La/ Al_2O_3 catalyst for the steam reforming of ethanol and phenol. They discovered that Ni disperses on the pure support, while La disperses in a disordered way and concurrently reduces the acidity of the support.¹³ Previous research reported on the effect of Rare-Earth component of the RE/Ni catalyst on the formation and nanostructure of SWCNTs.¹⁸ Several elements, including La, have been used together with Ni in bimetallic catalysts for the synthesis of SWCNTs.¹⁸⁻²² The bimetallic catalysts have been found to have synergistic effects in the

formation of SWNTs. The addition of rare-earth elements into the catalysts was often found to greatly improve the yield of SWNTs and even influences the nanostructure of the SWNTs, such as diameter and helicity.¹⁸ Reports of the role of co-loaded metals in the bimetallic catalysts ranged from one metal (Y) being separated from the other (Ni) with only Ni catalysing the growth process, through one metal associated with the CNM root development and the other supporting the growth of the CNMs to one metal serving as a precursor of a CNM nucleus and the other promotes growth. However, the exact roles played by catalyst metals in the formation of CNMs are still uncertain, and further studies are needed to obtain a clear understanding growth by co-loaded or bimetallic catalysts.

In our previous studies, nanosized particles of La and Ni were separately loaded on RANR to give La/RANR and Ni/RANR catalysts respectively (**Chapter 4, Section 4.4.2**). The catalysts were used in the synthesis of SCNMs via CVD (**Sections 5.3.2 and 6.3.2**). The La/RANR catalysed the synthesis of simple CNFs while Ni/RANR synthesized twisted CNFs where it usually catalysed synthesis of coiled carbon nanotubes (CNTs) over free floating Ni nanoparticles or Ni loaded on other support materials such as alumina, silica, ferric oxides and many others. Single transition metals such as Ni, Co and Fe have been used in the preparation of SCNMs.^{23,24} However, further research revealed that transitional mixed-metal components are more effective than single metals as catalysts. It was also found that incorporating a rare-earth element will give rise to a strong influence on both the quantity and the nanostructure quality of the SCNMs produced.²⁵

Here we report on the catalytic performance of La and Ni nanoparticles supported simultaneously on RANR to give a La-Ni/RANR co-loaded catalyst, which has not previously been studied as a catalyst for the synthesis of carbon nanomaterials. The synergistic effect of the La and Ni nanoparticles in the co-loaded catalyst was compared and contrasted against the performance of the individual catalysts under uniform CVD conditions. The stability of the catalyst, mechanism of CNMs growth and the properties and characteristics of the ‘as synthesized CNMs’ was explored with a hope of suggesting possible applications and scaling up for increased mass production.

In this work we also report the synthesis of SCNMs over co-loaded La-Ni/RANR catalysts in a CVD reaction. The La to Ni metal ratios was equal in the La-Ni/RANR catalyst material. However, the wt. % loading on the RANR support was varied from 1-10 wt. %. A parametric

study was then performed in which time of synthesis, temperature and H_2/C_2H_2 gas mixture flow rate was varied during the CVD synthesis. An optimal range of catalyst compositions and settings for the synthesis of SCNMs was determined from the different sets of parametric conditions.

8.3 Experimental

8.3.1 Preparation of supported La-Ni/RANR co-loaded catalysts

The support was prepared in a hydrothermal method in which titanium tetrachloride ($TiCl_4$), obtained from Sigma Aldrich was dispersed in water and refluxed for 24 h to produce RANR at 200 °C as outlined in **Section 4.3**. The La-Ni/RANR co-loaded catalyst was prepared using a simultaneous DPU method of synthesis (**Section 4.3.2**). Both lanthanum trichloride ($LaCl_3$) and nickel nitrate trihydrate ($Ni(NO_3)_2 \cdot 3H_2O$) were simultaneously and gradually added to a solution consisting of RANR suspended in a measured volume of deionised water. DPU was used to simultaneously load the La and Ni metals in their respective calculated weight percentages. Loadings of 1, 2, 5, 8 and 10 wt. % were achieved to give La-Ni/RANR catalysts. The DPU experiment was carried out at 80 °C for 24 h with vigorous stirring.

8.3.2 Synthesis of CNFs

Fig. 3.1 (see **Section 3.1.4**) shows the set-up of the CVD process used in the synthesis of CNFs in a horizontal quartz tube reactor. The co-loaded La-Ni/RANR catalyst was placed in a quartz boat positioned at the centre of the furnace. The temperature maintained at the centre of the furnace was varied at 300, 400, 500, 600 and 700 °C. Acetylene gas (C_2H_2) was introduced into the tube reactor at a flow rate varied at 50, 75 and 100 mL min⁻¹ with hydrogen set at the same flow rate being used as a carrier gas. The furnace's temperature was ramped up at a heating rate of 10 °C min⁻¹ to the pre-set reaction temperature and was held at that temperature for a pre-set period of time. The time period over which the CVD reaction ran was varied at 30 min, 1h and 2 h. C_2H_2 and the carrier gas H_2 were both introduced via their respective inlet tubes at a uniform pre-set flow rate. The furnace was allowed to cool down naturally to room temperature under hydrogen gas which was allowed to flow throughout the duration of the reaction. The parametric study for the synthesis of CNFs was conducted as outlined in **Scheme 1** of **Section 6.3.2**.

8.3.3 Characterisation of catalysts and carbon products.

The crystallographic phases of co-loaded La-Ni/RANR catalysts were determined by obtaining powder X-ray diffraction (PXRD) patterns using Bruker D2 Phaser diffractometer in a 2θ range from 7 to 120° using Co K α radiation wavelength (λ) of 1.79 nm. The “as-synthesized” CVD products were collected and analysed by transmission electron microscopy (TEM), scanning electron microscopy (SEM), and LRS. For TEM analysis, the samples were prepared by dispersing a small amount of the materials in methanol with slight sonication. The drops of the dispersed material were placed on a Cu grid. A FEI TEM Spirit operated at a voltage of 120 kV was used. For SEM analysis, the material removed from the tube reactor was directly mounted on a carbon tape on a sample holder stub. A FEI ZEISS FIB was used for SEM observation. The average particle size was determined using ImageJ and statistical analysis on TEM and SEM micrographs. A minimum of 200 particles were counted on the micrographs and using the normal Gaussian curve, the particle sizes were statistically confirmed. Energy-probe microanalysis (EPMA) was used to determine the chemical composition density of the carbon nanomaterials and the spatial distribution of materials in the La-Ni/RANR catalyst by EPMA WDS mapping and profiling.

8.4 Results and discussion

Deposition–precipitation using Urea (DPU) method efficiently loaded the metal nanoparticles on the RANR support to give La-Ni/RANR co-loaded supported catalysts. Metal wt. % loading ranging from 1-10 wt. % were achieved. Detailed analysis and characterisation of the catalysts using PXRD and EPMA revealed the crystallographic phases of the catalysts and the spatial distribution of the La-Ni nanoparticles on the RANR support respectively. The morphology of the supported catalysts and the CVD products was analysed using TEM and SEM from which the properties and characteristics of the catalyst materials and the carbon nanomaterials was studied in details. The varied parametric conditions of synthesis produced carbonaceous materials of distinct crystallinity. LRS measured the degree of disorderliness and graphicity in the carbon matrix of the carbon nanomaterials. Thermogravimetric analysis (TGA) revealed intrinsic details on both the catalysts and CNMs through thermal stability determinations.

8.4.1 PXRD and EPMA analysis

The dominant peaks observed in the PXRD patterns in **Fig. 8.1** are due to the rutile phase of the RANR support. The major peak of the rutile phase is occurring at 2θ 32.5° with crystal planes 110, while minor peaks occurred at 101, 200, 111, 211, 220, and 002. This trend was exhibited in the whole metal percentage loading range. This is because the rutile is in great abundance as the catalyst support. G. S. Gallego *et al.* reported that the La and Ni phases exist as La_2O_3 and NiO , the thermodynamically stable phases, which occur at the reduction temperature of the respective oxide materials.²⁶ The peaks identified as La in **Fig. 8.1** may be ascribed to $\text{La}(\text{OH})_3$ and La_2O_3 phases. These phases reduce to La at 600°C to give a co-loaded catalyst La-Ni/RANR. The peaks due to La occurring at 2θ values $< 30^\circ$ are increasing in intensities with an increase in La wt. % loading as shown in **Fig. 8.1**.

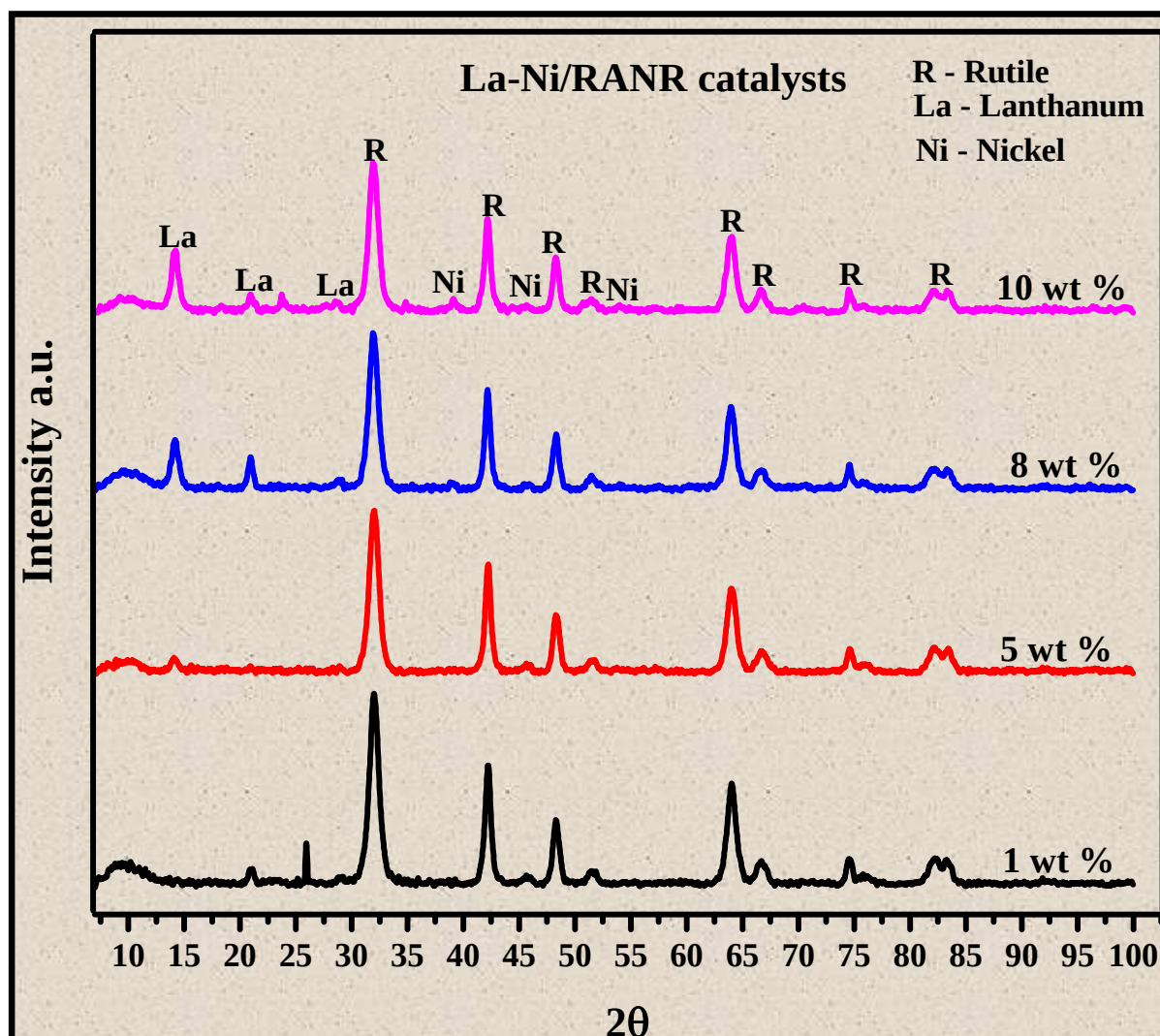


Figure 8.1: PXRD patterns of La-Ni/RANR co-loaded catalysts.

The occurrence of individual La and Ni phases shows that the metal nanoparticles are not in a mixed-metal system. However, calcination and reduction is postulated to facilitate the formation of the active La and Ni metallic nanoparticles in the La-Ni/RANR co-loaded catalysts.²⁷ The occurrence and distribution of the catalyst metal phases was analysed using wavelength dispersive spectroscopy mapping (WDS) by electrode probe microanalysis technique (EPMA) as shown in **Figs. 8.2 and 8.3**.

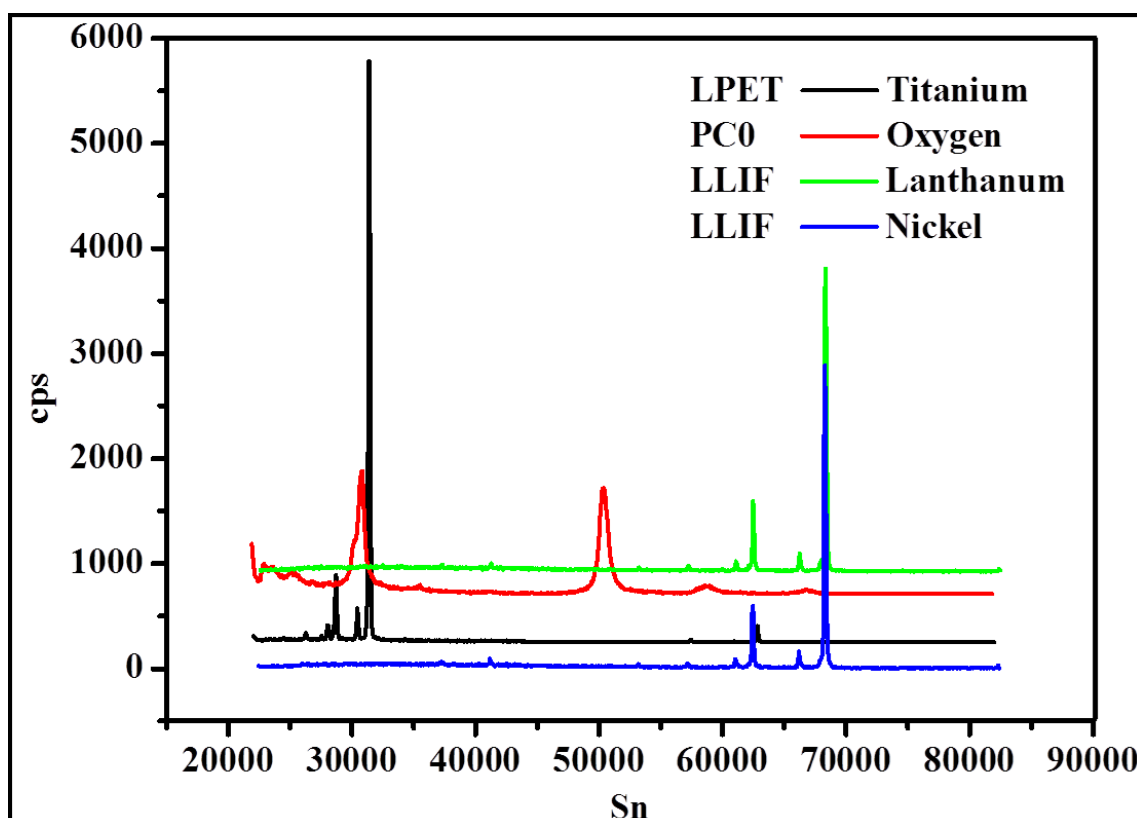


Figure 8.2: WDS spectrum profile of 10 wt. % La-Ni/RANR supported catalyst.

The characteristic X-rays convolute with the instrumental response to produce a WDS X-ray spectrum as shown in **Fig. 8.2** for the 10 wt. % La-Ni/RANR supported co-loaded catalysts. The X-ray spectrometer that measures the characteristic X-ray peak intensities was also set to measure count rates of the characteristic X-rays. The WDS spectra in **Fig 8.2** shows the peaks from the characteristic X-rays measured against the respective analysing crystals to their Bragg diffraction characteristics. The elements Ti, La and Ni are showing sharp high intensity peaks while the oxygen has two low intensity broad peaks. The distinct oxygen peaks are attributable to those from the TiO_2 support and the residual oxygen in the La and Ni of the co-loaded metal oxide nanoparticles. It was also observed that there are no significant peaks due to intermediate phases. The spectral pattern is comparable to the intensities

presented in the PXRD patterns of the La-Ni/RANR presented in **Fig. 8.1**. The X-ray intensity distributions of the elements from an X-ray map permitted generation of 2D and ternary scatter diagrams that present spatial information into concentration dimensions that display spatial relationships of elements or phases in materials.²⁸

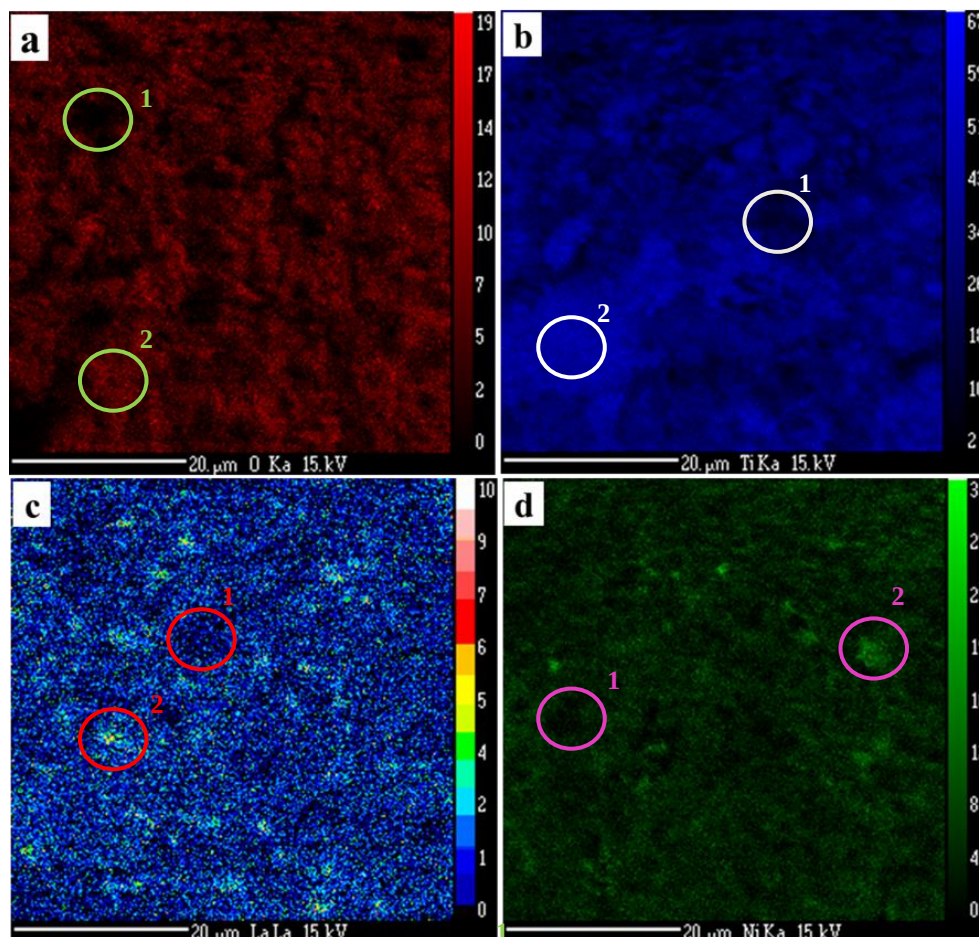


Figure 8.3: WDS spectral maps of 10 wt. % La-Ni/RANR supported catalyst. Elemental quantitative compositional maps of (a) O, (b) Ti, (c) La and (d) Ni of the bulk La-Ni/RANR mixed-metal catalyst.

WDS spectrometry was used to construct X-ray images of the sample showing the spatial distribution of each element in the La-Ni/RANR co-loaded catalyst. The element that generated higher counts from a more cross-sectional scattering resulted in a map showing high density distribution of the element on the map. The WDS spectral maps in **Fig. 8.3** show O, Ti, La and Ni-rich phases in which other elements of the catalyst do not exist. The oxygen map in **Fig. 8.3 (a)** is less dense as compared to those of La, Ti and Ni, a phenomenon correlated to **Figs. 8.1** and **8.2**.

The circled areas in **Fig. 8.3 (a) – (d)** showed examples of regions of low (1) and high (2) concentrations of O, Ti, La and Ni atoms respectively. A closer look at the maps showed that the elements are dispersed and concentrated on different points in the maps. However, the La map shows many brighter regions, a phenomenon attributable to its heavy atomic mass of 139 g mol^{-1} . The elemental maps of nanosized metal particles could be developed on a $20 \text{ }\mu\text{m}$ scale because the metals are supported on the μ -sized scale RANR. It can be concluded that both PXRD and EPMA analyses indicate that individual La and Ni phases co-exist in the La-Ni/RANR catalyst material. TEM micrographs in **Section 8.4.3** also shows how clustered the metal nanoparticles are on the RANR support at 10 wt. % loading.

8.4.2 Temperature programmed reduction (TPR)

Reduction profiles of the La-Ni/RANR catalysts provided intrinsic information about the behaviour and chemical interactions of the nanosized metal particles in the co-loaded system. **Fig. 8.4** shows the TPR profiles of the La-Ni/RANR catalysts at different wt. % loadings. The catalysts were all calcined at $700 \text{ }^{\circ}\text{C}$ in air for 2 h. The reduction peaks shifted to higher temperatures with an increase in metal nanoparticles wt. % loading. The intensities also increased with wt. % loading. This implied that the higher the wt. % loading, the more homogeneous was the metal-metal pairing and the orderliness in the La-Ni array. Consequently, the La-Ni nanoparticles attained higher crystallinity as confirmed by narrower and sharper PXRD peaks in **Fig. 8.1** and hence a higher reduction temperature of the La-Ni/RANR catalysts.

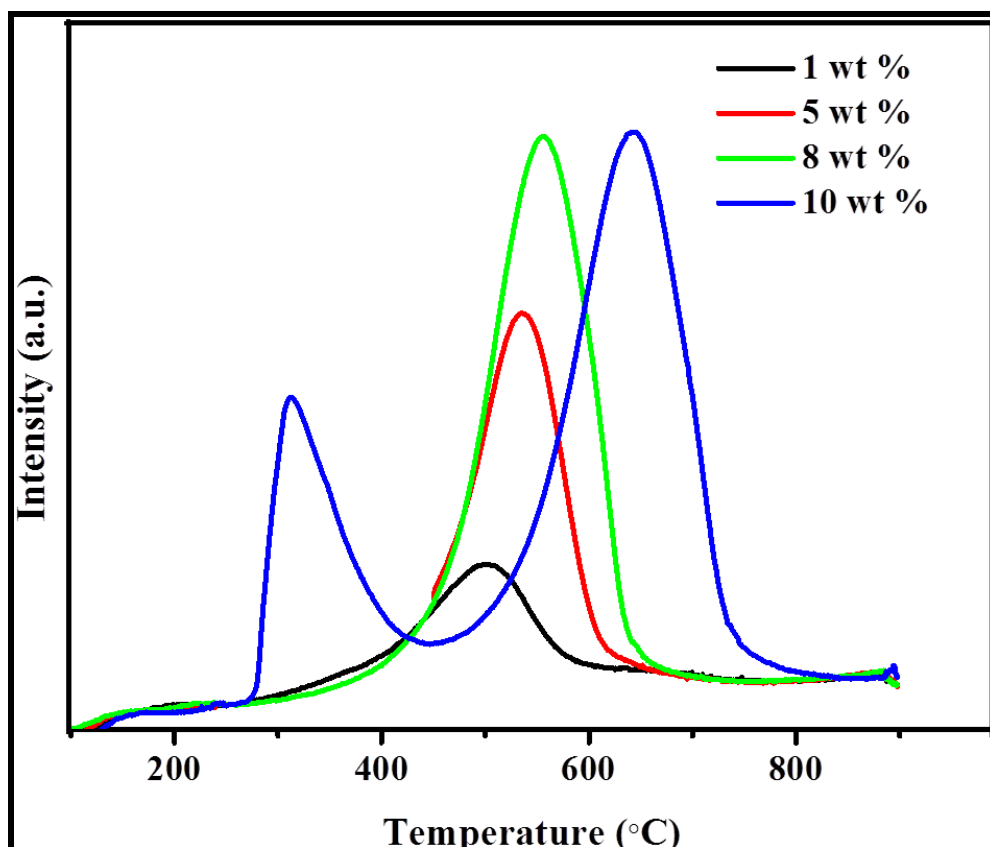


Figure 8.4. TPR curves of the La-Ni/RANR catalysts at different wt. % loadings calcined at 700 °C: 150 mg; gas flow rate: 5% H₂/Ar, 50 mL/min.

The reduction process completely reduced the oxide phases of the Ni and La to form the La-Ni co-loaded on RANR. The reduction profiles of catalysts at 1, 5 and 8 wt. % loading shows a single peak at 500, 540 and 580 °C respectively. The 500 °C reduction temperature for 1 wt. % La-Ni/RANR is comparable to that of plain RANR and the supported Ni/RANR (**Fig 4.10**). The reduction temperatures of Ni/RANR and La/RANR are 500 and 600 °C across all the wt. % metal loading range (see **Section 4.4.6**). However, the reduction temperatures observed for the La-Ni/RANR (**Fig. 8.4**) is a shift from that of the individually loaded catalysts. The peak positions shifted to higher temperatures due synergistic effect of oxides in different matrices in their respective metals on the surface of the RANR support material. Consequently, the increase in the oxygen in the metallic matrix of the catalysts increased the reduction temperature of the La-Ni/RANR compared to that of Ni/RANR and La/RANR at 500 and 600 °C respectively (**Fig 4.10b and c**). This consequently increased the reduction temperature as the wt. % loading increased as also confirmed by PXRD patterns showing increased intensities with increase in metal wt. % loading.²⁹

The catalyst at 10 wt. % loading has a TPR profile showing two peaks. Detailed studies showed that the peak at around 300 °C is not due to any of the metal oxide phases identified in the PXRD analysis, but it could be attributed to excess oxygen in the oxygen saturated NiO – La₂O₃ array on the rutile nanorod support surfaces of RANR.³⁰ The peak occurring around 680 °C corresponds to the complete reduction of the mixed-metal oxides in a one step process to give supported La-Ni/RANR mixed-metal catalysts.³¹ The high reduction temperature observed at higher wt. % metal loading is predominantly a consequence of increased metal-metal interactions in the metal-metal system. Morphological studies of the metal/-metal catalysts supported on the RANR using TEM and SEM gives detailed information on the physical nature of the metal nanoparticles that influenced their intrinsic behaviour and characteristics.

8.4.3 Transmission and Scanning Electron Microscopy

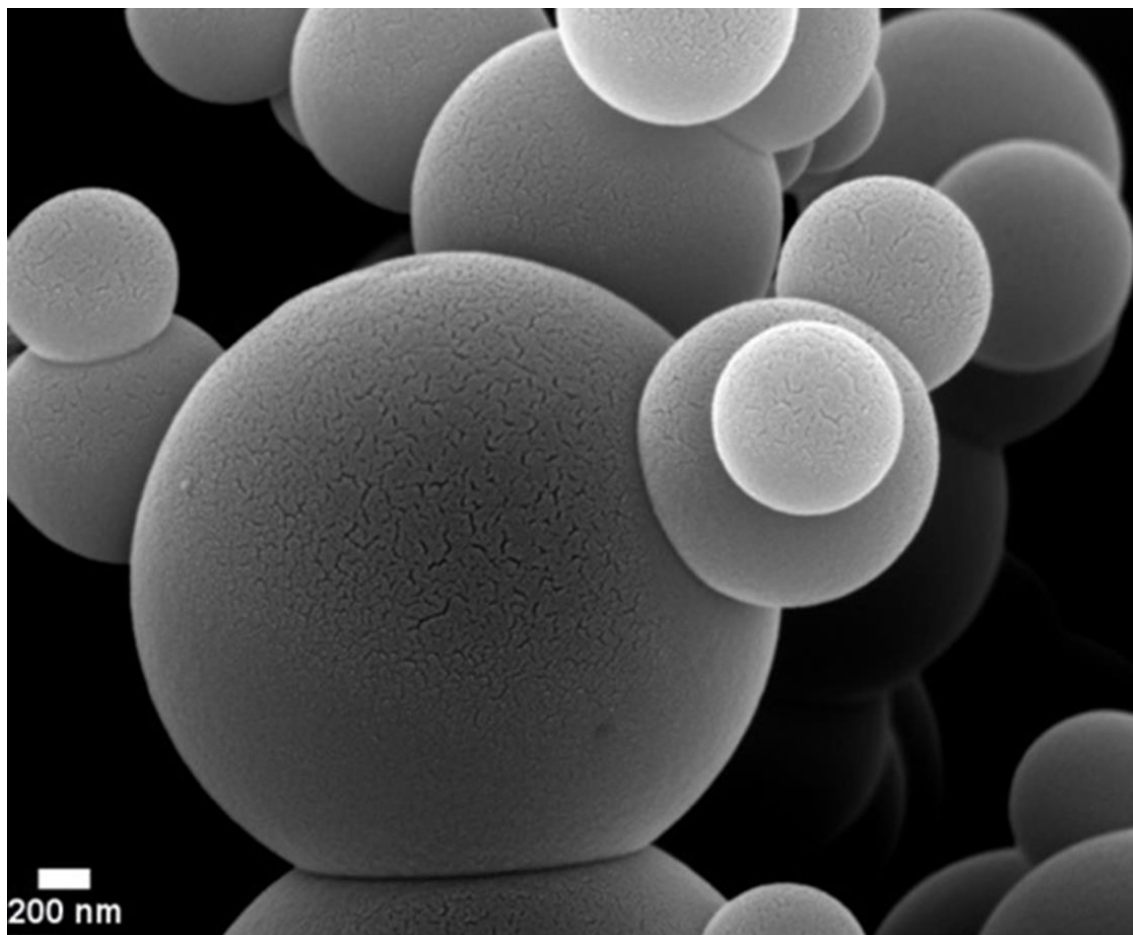


Figure 8.5: SEM micrograph of RANR prepared using a hydrothermal method at 200 °C over 24 h.

The morphology of the RANR support is characterised by spherical shapes formed from radially aligned rutile nanorods to form RANR microspheres. **Fig. 8.5** shows the

heterogeneously sized RANR with radii ranging from 50–600 nm. The micrograph suggests a tightly bound rutile nanorods network held at the centre of the RANR structure. The RANR exhibit high density mesoporous surfaces and this is expected to promote accessibility of the inner surfaces of the nanorods network. **Fig. 8.6** shows TEM micrographs of RANR supporting La-Ni nanoparticles of the La-Ni/RANR supported catalysts. The catalysts in micrographs of **Fig. 8.6** showed that at different wt. % loadings, the particles deposited on the support take different shapes and sizes. **Fig. 8.6 (a)** is a micrograph of 1 wt. % La-Ni/RANR showing polydispersed La-Ni nanoparticles on the RANR support, assuming a short rod-like structure. The particle size of the nanoparticles ranged from 2–10 nm with an average size of 4.9 nm.

The morphology of the La-Ni nanoparticles changed at higher percentage composition. **Fig. 8.6 (b)** is a TEM micrograph of 10 wt. % La-Ni/RANR showing La-Ni nanoparticles of different morphologies and sizes. The catalyst is showing agglomeration on the support surface suggesting extensive polydispersion of the La-Ni nanoparticles. This is a sharp difference at lower wt. % loadings as shown in **Fig. 8.6 (c)** which are characterised by less agglomeration and polydispersion of the La-Ni nanoparticles. Previous studies elucidated the presence of spherical particles of Ni in the 5 wt. % Ni/RANR (see **Chapter 6, Section 6.4.1**), with a diameter range of 1–6 nm with an average diameter of 4 nm while that of La (see **Chapter 5, Sections 5.4.2**), ranged from 2–8 nm with an average diameter of 7 nm. This is within the particle size range of the low wt. % loading of 1 wt. % La-Ni/RANR. It was observed that wt. % loading, the particle size range of La-Ni/RANR shifted to a longer range as presented in **Fig. 8.7 (a)**. This is comparable to the particle size distribution of the La-Ni nanoparticles on RANR which has a narrow range and a small average particle size of about 5 nm at 5 – 10 wt %.

The narrow range of particle sizes of the La-Ni mixed-metal catalysts is the synergistic effect of both the unique topology on RANR support and the DPU method of metal loading used. This synergy supports the loading of a very narrow range of nanosized metal particles on the support. The defects on which the metal particles sit on the RANR nanorods are yet to be studied to understand the actual mechanism of metal deposition. However, **Fig. 8.7** compares the particle size distribution of the La-Ni mixed-metal particles relative to the RANR nanorods thickness.

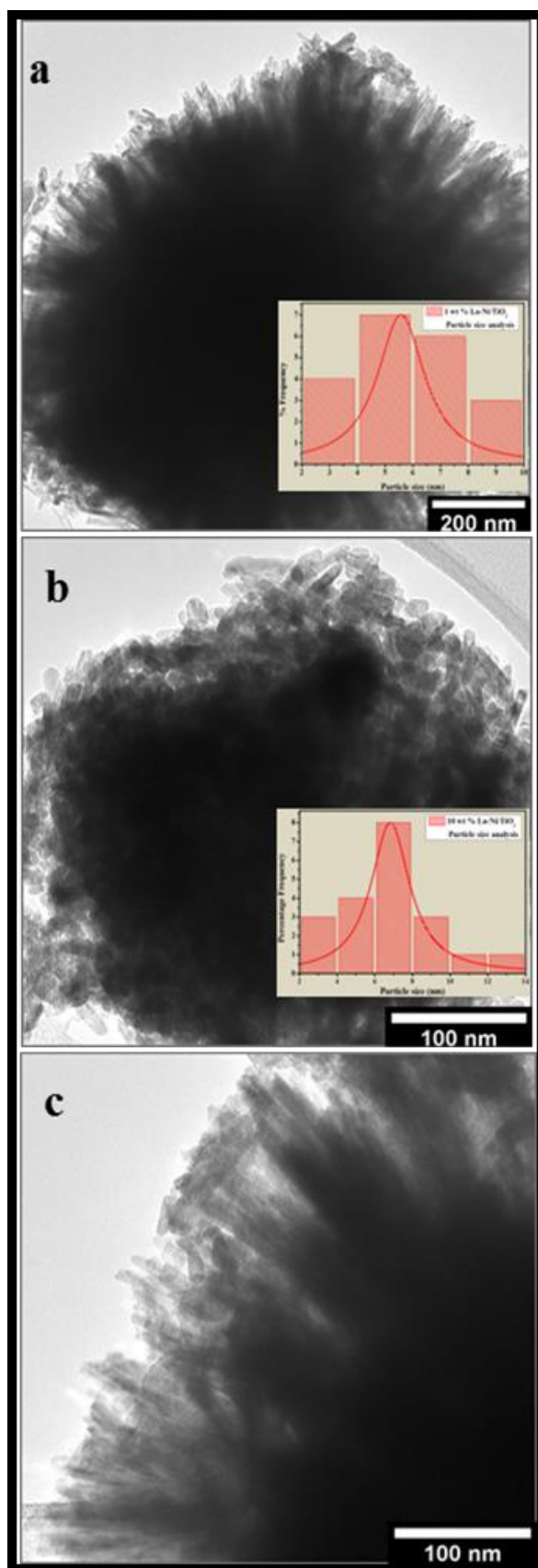


Figure 8.6: TEM micrographs of La-Ni nanoparticles co-loaded on RANR to give (a) 1 wt. % La-Ni/RANR(b) 10 wt. % La-Ni/RANR (c) 8 wt. % La-Ni/RANR supported catalysts.

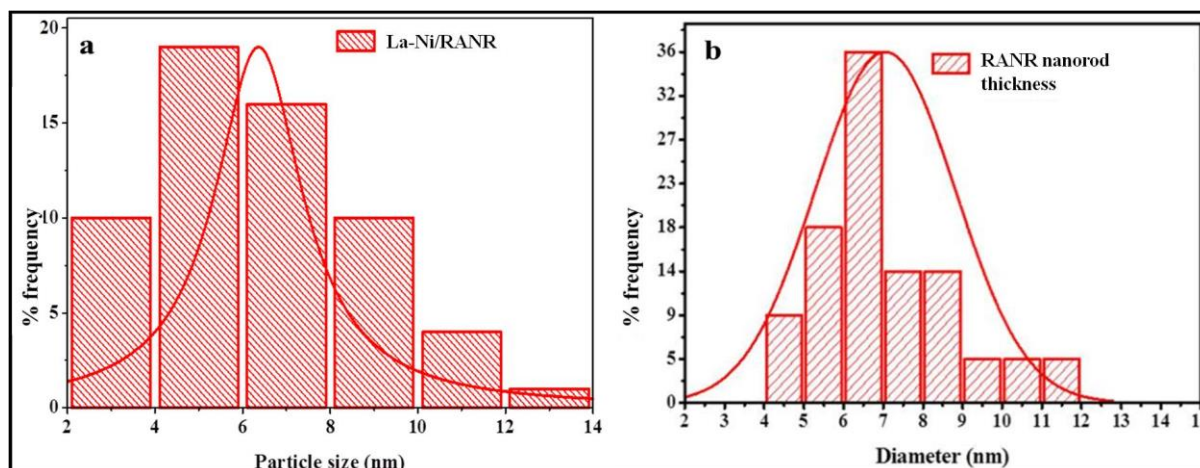


Figure 8.7: Size distribution analysis of (a) La-Ni nanoparticles supported on the RANR support (b) rutile nanorods of the RANR support.

The particle size analysis in **Fig. 8.7 (a)** shows a wider size range than the range of thickness of the rutile nanorods of the RANR support. However, the average size of the metal particles is about 6 nm while that of the rutile nanorods is about 7 nm. The few La-Ni particles with sizes greater than 10 nm may be attributed to agglomeration during DPU process and the subsequent calcination. This explains what is exhibited in **Fig. 8.6 (b)** in which the whole RANR sphere appears to be completely covered by La-Ni nanoparticles on its surface. The agglomerated particles of La-Ni and Ni appear as dark spots on the catalysts material. These properties and characteristics of the La-Ni nanoparticles and the supported La-Ni/RANR catalyst directly affected and influenced the nature of the carbon nanomaterials synthesized over these catalysts in CVD reactions. **Fig. 8.8** shows SEM micrographs of the carbon nanomaterials synthesized over La-Ni/RANR under different parametric conditions of varied wt. % composition, temperature, flow rate and time. Percentage weight composition was varied at 0.5 – 10 wt. % and a temperature of 300–700 °C over a time range of 30 min – 2 h with a flow rate of 50 – 1 00 mL min⁻¹.

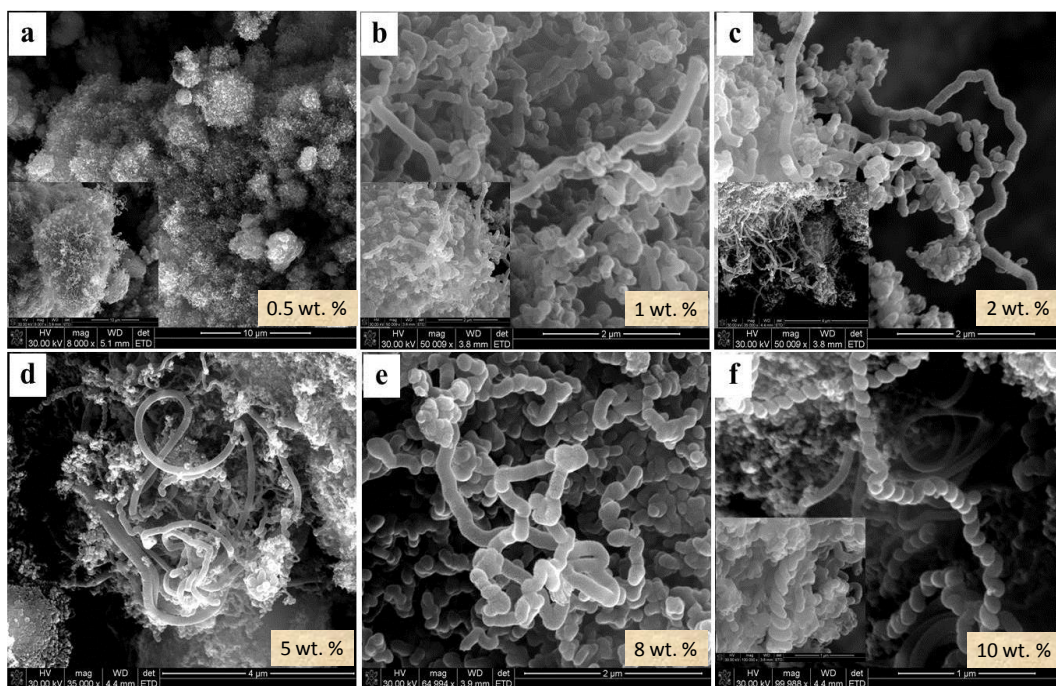


Figure 8.8: SEM micrographs of CNFs synthesised over 0.5 – 10 wt. % La-Ni/RANR at 500 °C, 1 h, 75 mL min⁻¹.

Morphological studies of the CVD products synthesized over the La-Ni/RANR catalysts performed using SEM revealed that the carbon nanomaterials are fibrous in nature. The CNFs are a mixture of both straight long fibres and twisted or coiled fibres. **Fig. 8.8 (a)** shows how the CNFs densely cover the RANR structure supporting the La-Ni nanoparticles. The CNFs also grew radially assuming arrangement of the radially aligned nanorods of the RANR support. It was postulated that the actual morphology of each individual CNF may have been directly attributed to the surface or end of the La-Ni nanoparticle over which it grew. This inferred that the straight CNFs (**Fig. 8.8 (d)**), were catalysed by the La end of the co-loaded La-Ni/RANR catalyst while the coiled or twisted CNFs (**Fig. 8.8 (f)**), were catalysed by the Ni end of this catalyst. This is in correlates with the observed CNMs synthesised over the mono-catalysts of La/RANR and Ni/RANR reported in **Chapters 5** and **6** respectively. The parameters varied during the CVD reaction had distinct influences on the products obtained. Temperature and wt. % loading significantly affected the yield due to relative temperature of catalytic decomposition to the C₂H₂/H₂ gas and hence degree of conversion over time periods. **Fig 8.9** presents TEM and SEM micrographs of CNFs synthesized at different temperatures.

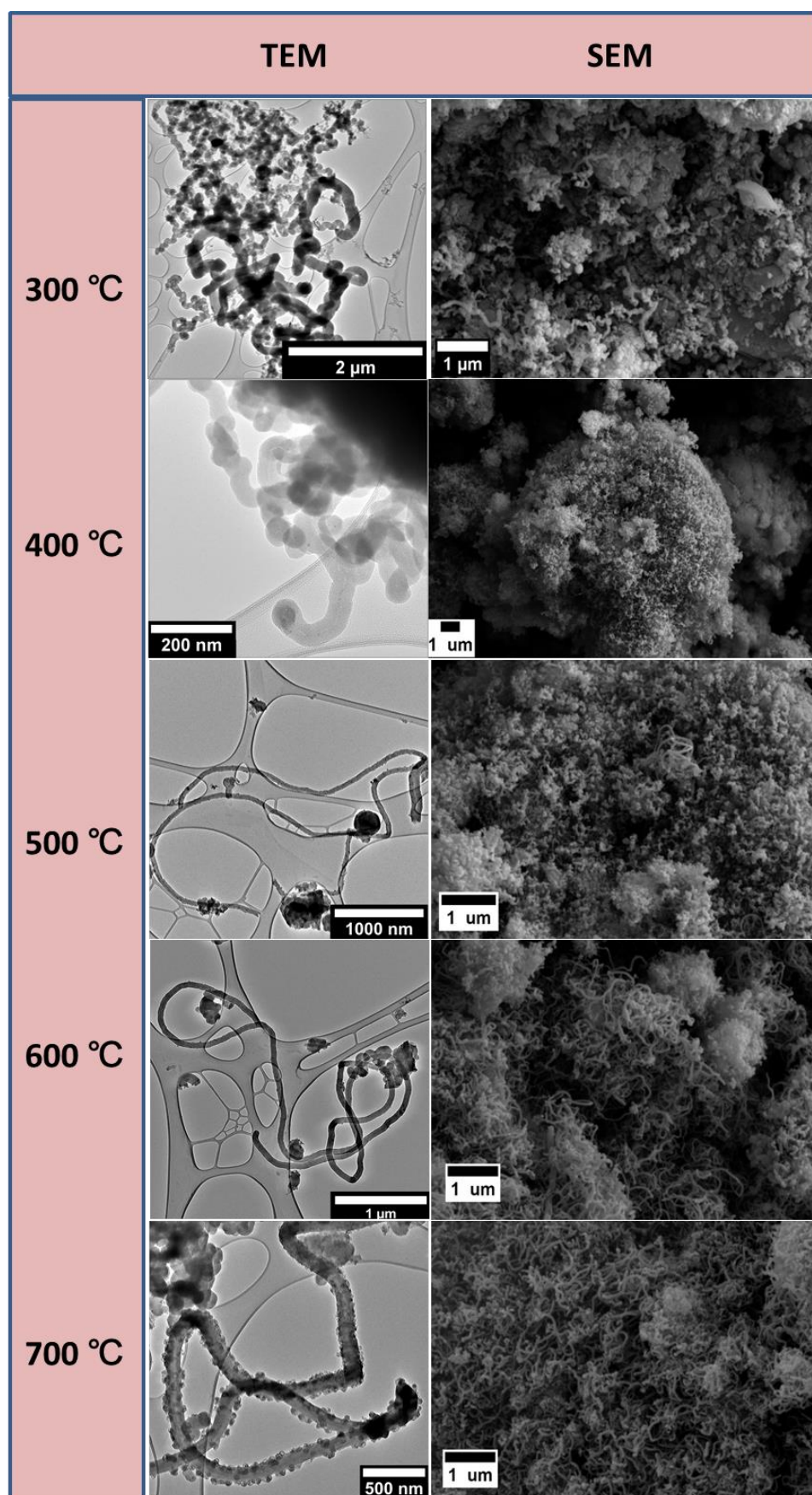


Figure 8.9. Twisted CNFs synthesized over 8 wt. % La-Ni/RANR at 1 h period and a flow rate of 75 mL min⁻¹ comparing temperature as a factor affecting CNFs growth per unit time.

Detailed studies showed similar trends at the whole wt. % loading, flow rate and time range. Temperature had the most significant influence due to its direct effect on the decomposition of C_2H_2 . The higher the temperature, the more efficient the C_2H_2 was decomposed and hence more catalytic conversion of the carbon generated into CNFs as shown in **Fig 8.9**. A closer look at the CNFs synthesised using TEM revealed that the fibres have twisted and straight chain morphologies.

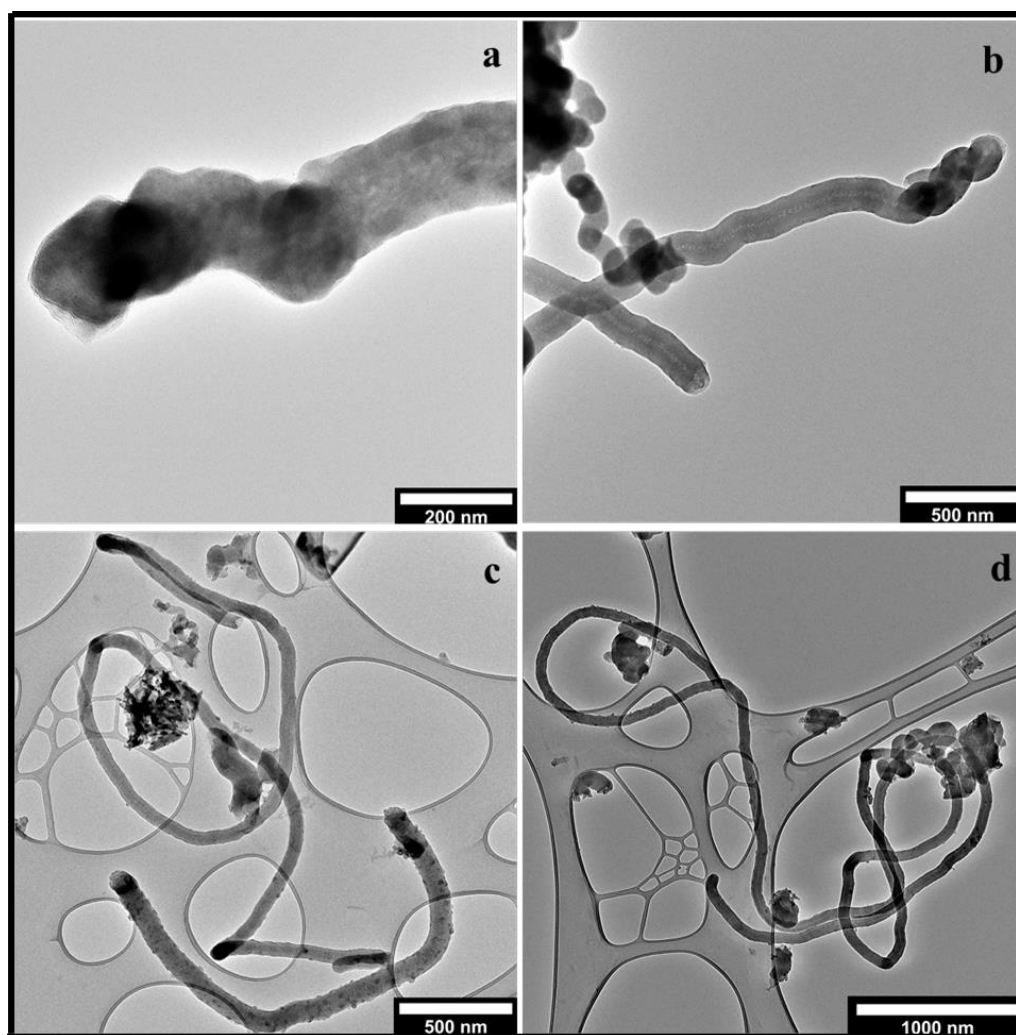


Figure 8.10: TEM micrographs of CNFs synthesised over La/RANR at (a) 1 wt. % (b) 2 wt. % (c) 5 wt. % (d) 10 wt. % all at 700 °C, 2 h, 100 mL min⁻¹.

TEM analysis of the CVD products also revealed that the La-Ni/RANR catalysed the synthesis of straight heterogeneous CNFs from C_2H_2/H_2 under different sets of parametric conditions. **Fig. 8.10** showed that the fibres are of a wide range of lengths and diameters. **Figs 8.10 (b) and (c)** shows fibres of different thicknesses while **Fig. 8.10 (d)** shows a single fibre

approximately 10 μm in length. The metal particle at the tip of some of the fibre plays a crucial role in determining the diameter of the synthesized fibres as explained in details in the previous chapters.

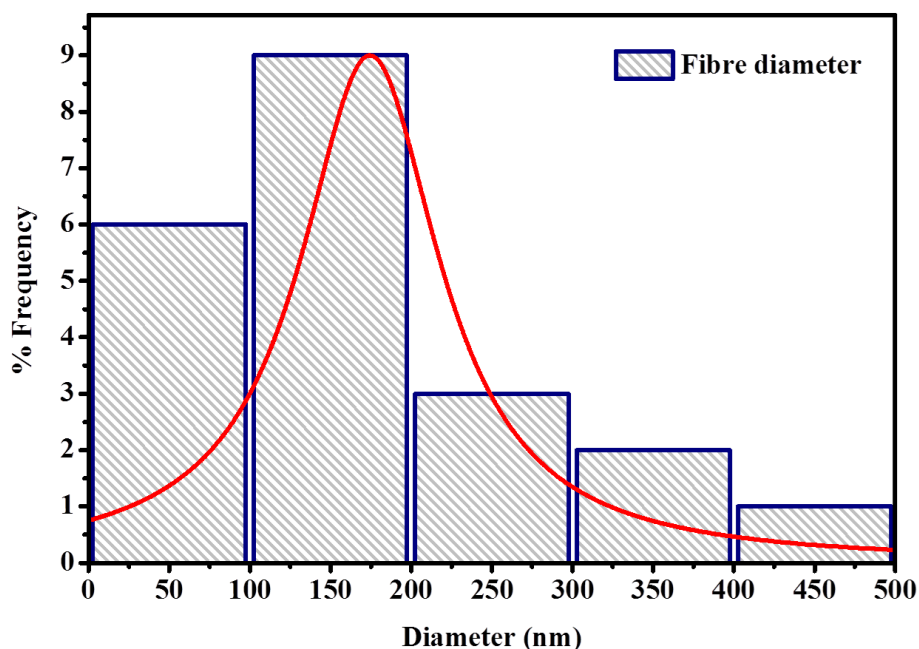


Figure 8.11: Fibre thickness distribution analysis of CNFs synthesized over 8 wt. % La-Ni/RANR catalysts at 1 h and a flow rate of 75 mL min^{-1} .

The CNFs synthesized over the La-Ni/RANR catalysts show a diameter range that is not comparable to the average particle size of the La-Ni nanoparticles of about 7 nm. This is because the metal catalyst particles have a tendency of agglomerating on the support surface as shown in **Figs. 8.2, 8.3** and **8.6**. This set the precedence for growth of thick CNFs. Moreover, the catalyst particles are dislodged from the point of support during CNF growth. Consequently, the metal catalyst particles undergo sintering during high temperature synthesis and give rise to the synthesis of even high diameter CNFs as shown by the data presented in **Fig. 8.11**. The fibres have a wide diameter range of 50–500 nm and an average diameter of about 175 nm. It can be concluded that the high diameter range is attributable to a widespread polydispersion of the La-Ni nanoparticles in the catalysts coupled with systematic increase in wt. % loading that promoted agglomeration and sintering resulting in the synthesis of CNFs of a high diameter range. The properties and characteristics of the CNFs synthesised over the co-loaded La-N/RANR were similar to those synthesised over the mono-loaded catalysts La/RANR and Ni/RANR at the whole parametric range. The following sections summarises the trends observed for the La-Ni/RANR co-loaded catalysts.

8.4.4 Percentage weight loading

The catalytic performance of the La-Ni/RANR was assessed by varying the percentage weight loading of the La-Ni nanoparticles on the RANR support. The catalysts were varied from 0.5–10 wt. %. Each catalyst was used under same set or parametric conditions. Two main observations were made. Firstly, the La-Ni nanoparticle size increased with an increase in wt. % loading as was observed in **Chapters 5 - 7**. This was because the RANR support remained the same in terms of its morphology, topology and the heterogeneous points at which loaded nanoparticles were deposited. As the percentage weight increased, the particles' proximity increased such that they became more susceptible to agglomerate at higher reaction temperatures. The catalyst materials tended to sinter and increased in particle size. At 10 wt. % loading, the La-Ni nanoparticles coverage density on the support is significantly high that TEM analysis showed a complete coverage of the RANR support (see **Fig. 8.6 (b)**). At lower wt. % loading, there is less or little agglomeration of La-Ni nanoparticles on the RANR support. However, it was observed that agglomeration took place as the La-Ni nanoparticles dislodged from the RANR support during CVD reaction.

The second observation was made on the influence of wt. % loading on the synthesis of CNFs in the CVD process. At all wt. % loading, the catalysts synthesized a mixture of straight and twisted CNFs with heterogeneous thickness and length under the whole range of parametric conditions. The general observation made was that average fibre diameter tended to increase with increase in wt. % loading. Since wt. % loading determined the coverage density of the La-Ni on the RANR support, the fibre coverage density on the RANR support was directly proportional to the degree of La-Ni nanoparticles distribution on the RANR support (see **Fig. 8.9**). It may be concluded that percentage weight loading only may not be used to characteristically explain the CNFs produced in the CVD process.

8.4.5 Effect of temperature on CNFs synthesis over La-Ni/RANR

Temperature plays a crucial role of assisting in the decomposition of the C_2H_2 used as the carbon source and providing the activation energy for the synthesis of the CNFs. However, detailed studies revealed that temperature also affect properties and characteristics of the CNFs produced (see **Chapter 5, Section 5.4.3**). It is expected that the outer diameter of the CNFs formed becomes larger with an increase in temperature. This is because increased reaction temperatures promotes sintering or agglomeration of catalyst nanoparticles and consequential gradual increase in particle size due to heat-induced aggregation during the reaction process (see **Chapter 6, Section 6.4.3**).³² This was observed in reactions involving

10 wt. % loading because of high density of catalyst particles at close proximity and readily aggregate to form agglomerated particles that facilitated synthesis of thick fibres (see **Chapter 7, Section 7.4.4**). However, at lower metal loadings, this phenomenon was minimal. TEM and SEM micrographs show how the catalyst particles agglomerate on the support surface and are further confirmed by TPR analysis. The degree of graphitisation and crystallinity of the CNFs increases with an increase in temperature as expounded in Raman studies (see **Chapter 6, Table 6.1**). At 700 °C the fibre thickness and crystallinity was observed to be high than in low temperature reactions at 300 – 500 °C.

8.4.6 Gas flow rates and time variation

Detailed studies on the effect of gas flow rate and time variation revealed that both parameters affect the CVD products in similar ways. At low gas flow rate or short time periods, very little carbon is available for deposition on the La-Ni nanoparticles surfaces (see **Section 5.4.4**). This implied that low yield carbon materials are produced and are mainly amorphous. This phenomenon is not affected by temperature variation because the little carbon deposited undergoes incomplete hybridisation and thus contributing to a disordered carbon matrix. The carbon materials consist of a mixture of sp^2 and sp^3 hybrid carbons that do not completely close graphite rings of the carbon material and hence made amorphous carbon products. At high flow rates and short time periods, amorphous carbon rapidly deposits on the catalyst material and the carbon is inadequately crafted into disordered products. But at low flow rates and long time periods, there is insufficient carbon for complete synthesis of CNFs (see **Section 7.5.4**). It was observed that at high flow rates and long time periods, the actual properties and characteristics of the CVD products are subject to temperature. This is because flow rate and time only determines how much carbon is deposited on the catalyst material. It is the nature of the catalysts and temperature that gives the CNF their intrinsic properties and characteristics by influencing the mechanism in which the CNFs are synthesized during the CVD reaction. It may be concluded that time or flow rate only may not be adequately used to account for the acquired qualities of the synthesized CNFs.

8.4.7 LRS analysis of CNFs synthesised over La-Ni/RANR

LRS studies enabled determination of detailed intrinsic characteristics and properties of ‘as-synthesized’ carbon nanomaterials. By measuring the modal points of the respective peaks of the Raman spectrum, diameter distribution may be determined from relative peak intensities while the spectral lines reveal the nature of the carbon nanomaterials prepared by analysing their tangential modes, G- band (1590 cm^{-1}) and compared to either the low-frequency peaks, D-band (1320 cm^{-1}) and or radial breathing modes ($140\text{-}190\text{ cm}^{-1}$).²⁵ Detailed studies of Raman measurements performed on CNFs synthesized over the whole range of La-Ni/RANR catalysts showed a common trend in the D and G-band peaks.

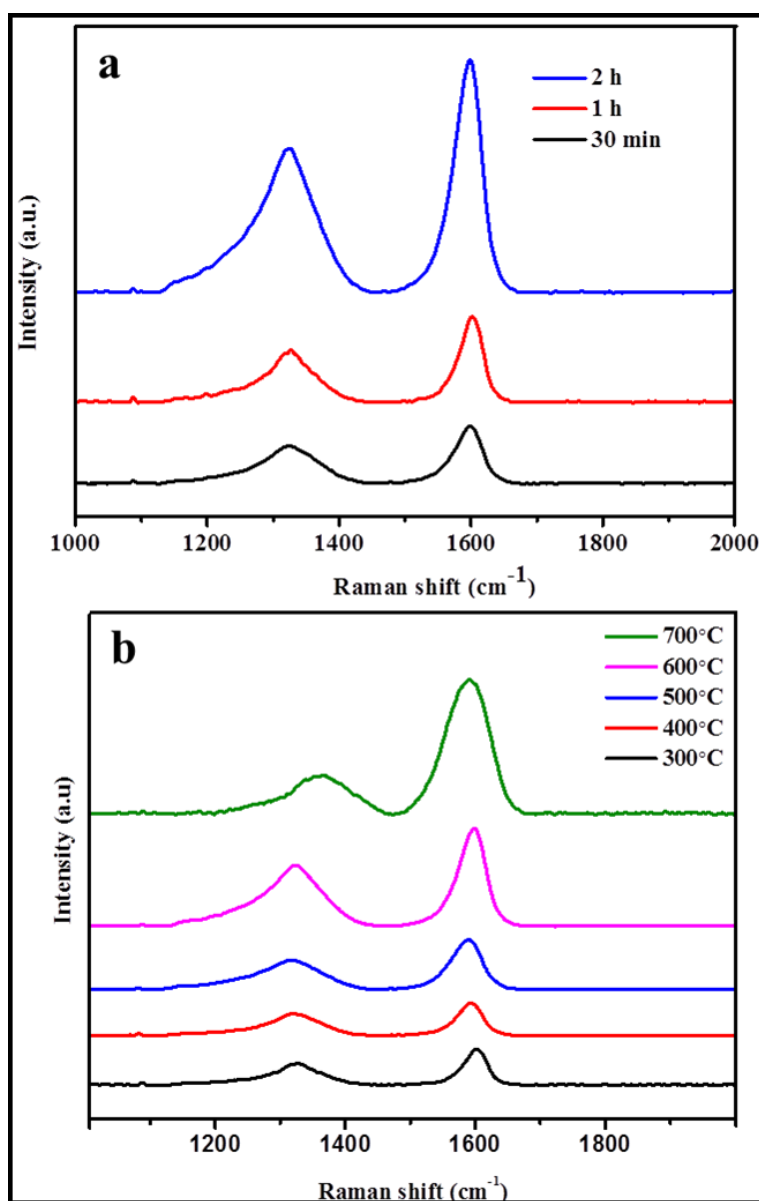


Figure 8.12: Laser Raman spectra of CNFs (a) Synthesized over 5wt. % La-Ni/RANR catalysts at different time periods, (b) Synthesized over 10wt. % La-Ni/RANR catalysts at different temperatures under uniform conditions (2 h, 100 mL min^{-1}).

The Raman spectra did not show low-frequency peaks due to carbon confirming that the catalysts did not synthesize single walled carbon nanotubes (SWCNTs) and hence all the materials produced are CNFs.³³ **Fig. 8.12** shows that the G-band is at 1600 cm^{-1} while the D-band is at around 1325 cm^{-1} . This suggests that the La-Ni/RANR catalysts have a strong consistent influence on the synthesis of the carbon network in both the straight and twisted CNFs.³⁴ **Fig. 8.12 (a)** shows the variation of peak intensities at different time periods of CNF synthesis. It can be observed that the intensities of both the D and G-band peaks increased with an increase in time. This is because as time increased, there was increased catalyst exposure to the carbon source. The carbon network nucleated into a more crystalline graphitic form giving rise to a high intensity G-band peak.³⁵ However, disorderliness occurs within the carbon matrix as a result of limited carbon interaction with the catalyst surface resulting in the D-band peak. The carbon is incorporated as amorphous carbon and causes defects in the CNF's matrix as is common in multiwall carbon nanotubes (MWCNTs) and defects in SWCNTs.³⁶ It can be concluded that the CNFs are more graphitic but with considerable disorderliness as confirmed by the G and D-band peak intensities respectively.

Temperature supports enhanced crystallinity in the synthesis of carbon nanomaterials coupled with the direct influence of the catalyst over which carbon growth is taking place. **Fig. 8.12 (b)** presents Raman spectra of CNFs synthesized at different temperatures with all other parametric conditions held constant. The D and G-bands are at 1325 and 1600 cm^{-1} respectively with the G-band more intense than the D-band peak. The Raman peak intensities also increased with increase in temperature from $300\text{--}700\text{ }^{\circ}\text{C}$. The spectra shows that there is no significant change in the main radial breathing mode peak positions over the $300\text{--}600\text{ }^{\circ}\text{C}$ temperature range. At $700\text{ }^{\circ}\text{C}$, the D-band peak shifted from 1325 cm^{-1} to around 1375 cm^{-1} and this may be explained in terms of temperature enhanced crystallinity as a consequence of low degree of disorderliness in the amorphous carbon (**Chapter 5, Section 5.4.3**). This peak shifting observed may indicate that the diameter of the CNFs is not affected by temperature but by particle size of the catalyst nanoparticles (**Chapter 6, Section 6.4.3**). However, the D-band peak-shift to the right at $700\text{ }^{\circ}\text{C}$ showed relative purity tendencies in the CNFs. This is because the less disorderliness there is in the carbon matrix of the CNFs, the more crystalline and graphitic they are and hence the pure the product. This is also comparable to the yield of the CNFs with temperature. It was observed that as temperature increased, the yield also increased because higher temperatures facilitate efficient decomposition of the C_2H_2 carbon source and make it readily available at the catalyst reaction

surface for CNFs synthesis. It may be concluded that there was no synergistic effect observed in La-Ni/RANR co-loaded catalysts. The trends explained in Sections 5.4.3 and 6.4.3 was also observed for the CNFs synthesised over La-Ni/RANR catalysts.

8.4.8 Thermogravimetric analysis (TGA)

Synthesis of CNFs over the La-Ni/RANR was measured using thermogravimetric analysis (TGA). The technique allowed the quantification of the amount of carbon deposited on the surface of the catalyst during the CVD synthesis of CNFs.²⁶ The analysis confirmed how the reaction parameters influenced and affected the production of CNFs over the catalyst materials. **Fig. 8.13** presented decomposition profiles of analyses at different time periods of CNFs synthesis (**Fig. 8.13 (a)**) and at different temperatures (**Fig. 8.13 (b)**). Time was varied at 30 min, 1h and 2 h. The profile of products synthesized at 30 min showed a weight loss of about 35 %. This increased to 45 and 50% for 1 and 2 h respectively. This implied that the longer the reaction time, the more CNFs that were synthesized over the catalyst material. This was because the catalyst was sufficiently exposed to the carbon depositing on its surface and allowed adequate synthesis of more crystalline carbon matrix of the CNFs. The CNFs synthesized at longer time periods tend to have a dense coverage around the catalyst (**Fig. 8.10 (a)**). Coupled with high temperatures, the CNFs tend to be of great length and have a thick outside diameter and hence a high weight loss during TGA analysis as shown in **Fig 8.13 (a)**. There is a measurable degree of correlation between the crystallinity of the CNFs and the TGA data.^{37,38} The insert in **Fig. 13 (a)** shows differential thermogravimetric curves (DTG) for the corresponding time variation TGA analyses. All the DTG profiles have major peaks above 550 °C which are ascribed to deposition of coke with different degree of crystallinity and graphicity over the La-Ni/RANR catalysts.³⁹ The DTG peak of CNFs at 30 min is showing a single peak at 650 °C while that at 2 h is at 680 °C. The 1 h profile is showing multiple peaks which are attributed to different phases of carbon such as monoatomic carbon and amorphous carbon which is highly unstable and reactive and hence decomposes at low temperatures < 550 °C. The residual weight is due to the La-Ni/RANR catalyst materials.

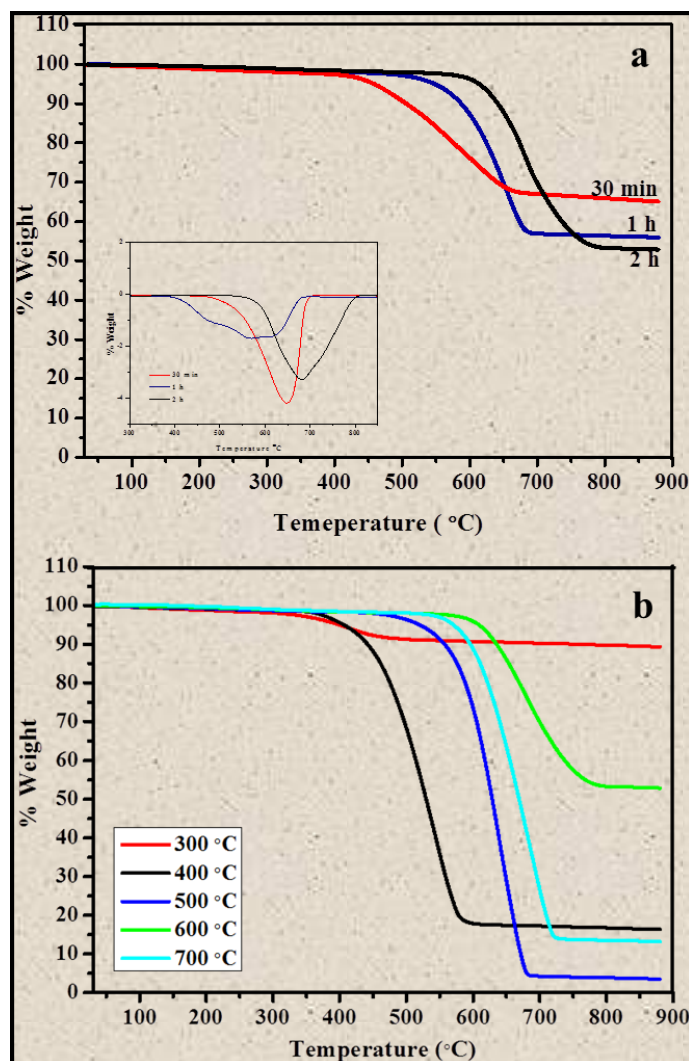


Figure 8.13: TGA profiles of CNFs (a) Synthesized over 1wt. % La-Ni/RANR catalysts at 600 °C and 75 mL min⁻¹ at different time periods, (b) Synthesized over 10wt. % La-Ni/RANR catalysts at different temperatures under uniform conditions (2 h, 100 mL min⁻¹).

The comparison of CNFs synthesized at different temperatures with all other conditions held constant using TGA revealed the quality of the CNFs and also the yield of the CVD reaction. **Fig. 8.13 (b)** illustrates the effect of temperature on the quality of CNFs synthesized by the La-Ni/RANR catalysts. Previous research reported that low-temperature TGA and TPO peaks are due to combustion of amorphous carbon species while peaks at higher temperatures could be attributed to graphitic carbon. The profile for products at 300 °C showed a weight loss of about 8 % and 92 % being due to residual catalyst material. This implied that at 300 °C, very little carbon material is deposited on the catalysts and the temperature is too low to support the synthesis of crystalline graphitic carbon material. At 400 °C, there is increased yield but the carbon materials are predominantly amorphous carbon that quickly burnt out at 400 – 580

°C with a weight loss > 80 %. Reactions at higher temperatures ranging from 500 – 700 °C show high graphitisation, increased yield and weight loss along this temperature range (**Fig 13 (b)**). We can conclude that temperature and wt. % determines the amount of carbon deposition on the La-Ni/RANR catalyst and the quality of the CNFs synthesized.

8.5 Conclusions

A two-step procedure of DPU followed by reduction afforded the preparation of La-Ni nanoparticles supported on RANR to give La-Ni/RANR mixed-metal catalysts. TPR and PXRD results proved and confirmed the mechanism of formation of the supported La-Ni/RANR catalyst through DPU and reduction. The wt. % loading affected the sizes of the La-Ni nanoparticles. The La-Ni/RANR catalysed the synthesis of a mixture of long straight chain CNFs and twisted CNFs using a simple CVD method. The La-Ni/RANR catalyst did not show intrinsic synergistic effect in its catalytic effect during the synthesis of CNFs. The different metallic ends catalysed fibres of different morphologies as was observed for the mono-loaded La/RANR and Ni/RANR catalysts in **Chapters 5** and **6** respectively. Reaction parametric conditions influenced the quality, properties and characteristics of the CNFs synthesized over the La-Ni/RANR catalysts. Raman and TGA analyses revealed that the CNFs were more graphitic but with considerable disorderliness as confirmed by the G and D-band peak intensities and TGA profiles respectively. Temperature and wt. % loading were proved to be crucial parameters that determine the amount of carbon deposition on the La-Ni/RANR catalyst and the quality of the CNFs synthesized.

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Chapter 9

Influence of nickel, gold and lanthanum metal nanoparticles on the photocatalytic performance of RANR

9.1 Introduction

Photocatalysis studies were carried out by assessing the photodegradation of coloured or dye chemicals such as methyl orange (MeO), phenolphthalein and other related dyes.¹ Materials that are activated by absorbing visible-light perform very well as photocatalysts. The wide scale study for photocatalysts takes place at the background of ever increasing new water pollutants and fast depletion of fresh water supplies.² This has set precedence for intensive research for alternative methods of water treatment and purification at minimum cost and reduced energy usage.³ TiO₂ has shown excellent photocatalytic behaviour.⁴ However, TiO₂ in its pure form can only be activated under UV light irradiation largely because of its wide band gap energy of approximately 3.2 eV.⁵ This phenomenon is however modified by extending the absorption edge to visible region by doping the TiO₂ with metal or non-metal elements that can effectively enhance the photoresponse and visible light photoactivity.^{6,7} However, there is no commercial product already using this solution mainly because the cost estimates of this technology has a treatment cost similar to that of current treatment methods such as granular activated carbon and ultraviolet light/peroxide accompanied by high destructive rates.⁸ Uniform light distribution inside the reactor is still difficult to achieve and providing and maintaining high surface areas of catalyst per unit reactor volume presents major challenges in the design of large-scale photocatalytic water treatment plant.⁹ Many transition metals are currently being investigated as materials to be loaded onto titania, primarily because of their band gap that improves electronic transitions between the TiO₂ and the metal catalyst it supports.

Loading of Au, Ni, La and La-Ni metal catalyst nanoparticles on RANR was reported in Chapter 4. DPU using urea was used to load the metal catalysts on the RANR support. A 500 W power input Newport 69911 solar simulator fitted with a 300 W Xe short arc lamp (Eurolux) with 3 W of radiant flux was used as a source of UV light for the photodegradation

of methyl orange (MeO). The lamp was kept at 20 cm from the quartz reaction vessel to afford a radiation of 100 W. m^{-2} .

9.2 Literature Review

The rutile phase TiO_2 has been used as a catalyst in photocatalytic reactions largely because of its inherent properties and characteristics.¹⁰ Some of the desirable properties of TiO_2 that make it a suitable material for photocatalysis include: physical and chemical stability, non-corrosive, and that it is inexpensive.¹¹ The photocatalytic activity of TiO_2 was reported in previous studies to be improved by doping it with different materials, including metals.^{5,12} Metal dopants used in photocatalysis are mainly of three types: transitional platinum group metals (PGMs), actinides and lanthanides.⁶

Transition metal elements are used in many catalytic reactions as the main active catalyst, a co-catalyst or catalyst support.¹³ The PGMs have been used as catalysts and co-catalysts.⁶ Metals such as Fe, Ta, Ni, V, Cr, W, Ce, La and Sm and non-metals such as F, B, S and C have been supported or co-doped on TiO_2 for photocatalysis applications.⁶ The metals have also been used as co-catalysts with La recently finding use in the synthesis of CNFs as presented **Chapter 5, Section 5.4.2** of this work. TiO_2 support nanoparticles have a tendency to agglomerate. The agglomerated TiO_2 nanoparticles tend to lose their nanosize and catalytic effect. Consequently, agglomerated catalyst particles are susceptible to build up high surface energy and become difficult to recycle on absorption of pollutant molecules.¹⁴ The co-catalysts then served reducing agglomeration by immobilising the TiO_2 nanoparticles and retain their nanosized particles during photocatalysis reactions.¹⁵ The choice of supported metal is based on the ability of the material to improve the photocatalytic efficiency by assisting in the charge separation of photogenerated electron-hole pairs and/or reduce the band gap of TiO_2 or effect surface Plasmon resonance (SPR).^{16,17}

The supported metals could serve in enhancing the photogenerated charge transfer at interface of the supported metal and the photocatalyst. The supported metals may also propagate the transfer process of the photogenerated charges at the photocatalyst - electrolyte interface. Previous studies of supporting Ni nanoparticles (NPs) on TiO_2 used for the photodegradation of MeO revealed that the ability of light absorption in the visible region was enhanced by an order of greater than 0.01 min^{-1} .⁷ The Ni expanded the spectral response of the TiO_2 nanotube arrays photocatalyst, due to the broad indirect band gap of Ni ($\sim 3.55 \text{ eV}$).^{16,18,19} However, Ni has the effect of collecting the photogenerated holes on the surface of

TiO₂ thereby promoting the separation of electron–hole pairs. Consequently, more holes can accumulate on the surface of TiO₂ to participate in the photocatalytic oxidation reactions. This implied that Ni was essential in decreasing the band gap energy between the Ti 3d and O 2p.^{20–22} Previous studies reported that the Ni²⁺ ion improved the photocatalytic activity of most semiconductor photocatalyst because the existence of Ni²⁺ suppresses recombination of electron-hole pair on the TiO₂ surface.²³

The efficiency of TiO₂ as a photocatalyst is maximised by improving its charge carrier separation during the photo-electrochemical and photocatalytic processes. Noble supported metals such as Au and Pt are known to modify the TiO₂ and bring about improved charge carrier separation and plasmonic effects.²⁴ Previous studies showed that AuNPs influence the performance of the TiO₂ photocatalyst by catalysing the recombination of photogenerated holes and electrons. It also affects the selectivity in the photocatalytic reactions.²⁴

La/TiO₂ is reported to exhibit higher photocatalytic activity when the catalyst is prepared by ultrasound-assisted sol-gel method.²⁵ In this work, the RANR structure was used to support Au, Ni, La and La-Ni co-loaded catalysts as explained in **Chapter 4**. The RANR structure is morphologically stable and does not undergo agglomeration at the temperature range under which photocatalysis is usually carried out (> 100 °C). However, the structure collapses at temperatures around 700 °C.

9.3 Experimental

The preparation and characterization of the catalysts materials used in this work was presented and explained in details in Chapter 4. The catalyst materials La/RANR, Ni/RANR, Au/RANR, La-Ni/RANR and plain RANR were used to determine the influence of the loaded metal nanoparticles on the photocatalytic performance of RANR.

9.3.1 Photocatalytic degradation of methyl orange (MeO)

In a quartz glass tube column, 0.01 g of each respective catalyst was dispersed in a 50 mL aqueous solution of 50 ppm methyl orange. The solution was kept under vigorous stirring throughout the experiment. The solar simulator fitted with a 300 W Xe short arc lamp was used as a source of light for the photodegradation of methyl orange (MeO). A monocrystalline silicon photovoltaic cell was used to set the solar simulator irradiance to 1 sun. The lamp was kept at 20 cm apart from the quartz reaction vessel to afford radiation of 1000 W. m⁻². The light was set to be perpendicular to the surface of the reactor. The

reaction vessel with its contents was homogenised by continuous stirring in the dark for an hour before visible light irradiation. Samples of 2 mL of the reaction mixture were drawn at 15 min intervals using a plastic disposable syringe fitted with a PVDF membrane filter. The aliquots had their concentrations measured on a Varian UV-Vis spectrophotometer. The rate of photodegradation was therefore monitored by observing the change in concentration of the MeO with time.

9.4 Results and discussion

9.4.1 UV-vis diffuse reflectance spectra (DRS)

The electronic interaction in photocatalytic materials influences the charge-transfer transitions particularly between activated catalysts and their respective support materials. The excitation of the electrons determine the magnitude of the transitions from the valence band to conduction band and hence enhances the absorption in the visible region. **Fig 9.1** showed the UV-vis diffuse reflectance spectra of the supported catalyst and the plain RANR. The plain RANR was observed to have a sharp absorption edge at around 380 nm ($E_{bg} \sim 3.2$ eV). The La, Ni and the co-loaded La-Ni/RANR catalysts show slight extended absorption spectra with the Au/RANR having a more significant expanded absorption. **Fig 9.1** shows that all the supported catalysts absorb in the same absorption band as that of RANR and they did not shift the band gap of TiO_2 .

The plain RANR and the supported catalysts all predominantly absorb in the UV-region. However, Ni/RANR shows a peak at 450 – 600 nm. This implies that Ni is bringing about absorption in both the visible and UV regions of the spectrum. Ni is reported to show enhanced visible-light photocatalytic activities as it tend to modify TiO_2 in visible region resulting in absorption originating from defects associated with oxygen vacancies that give rise to coloured centres.⁷

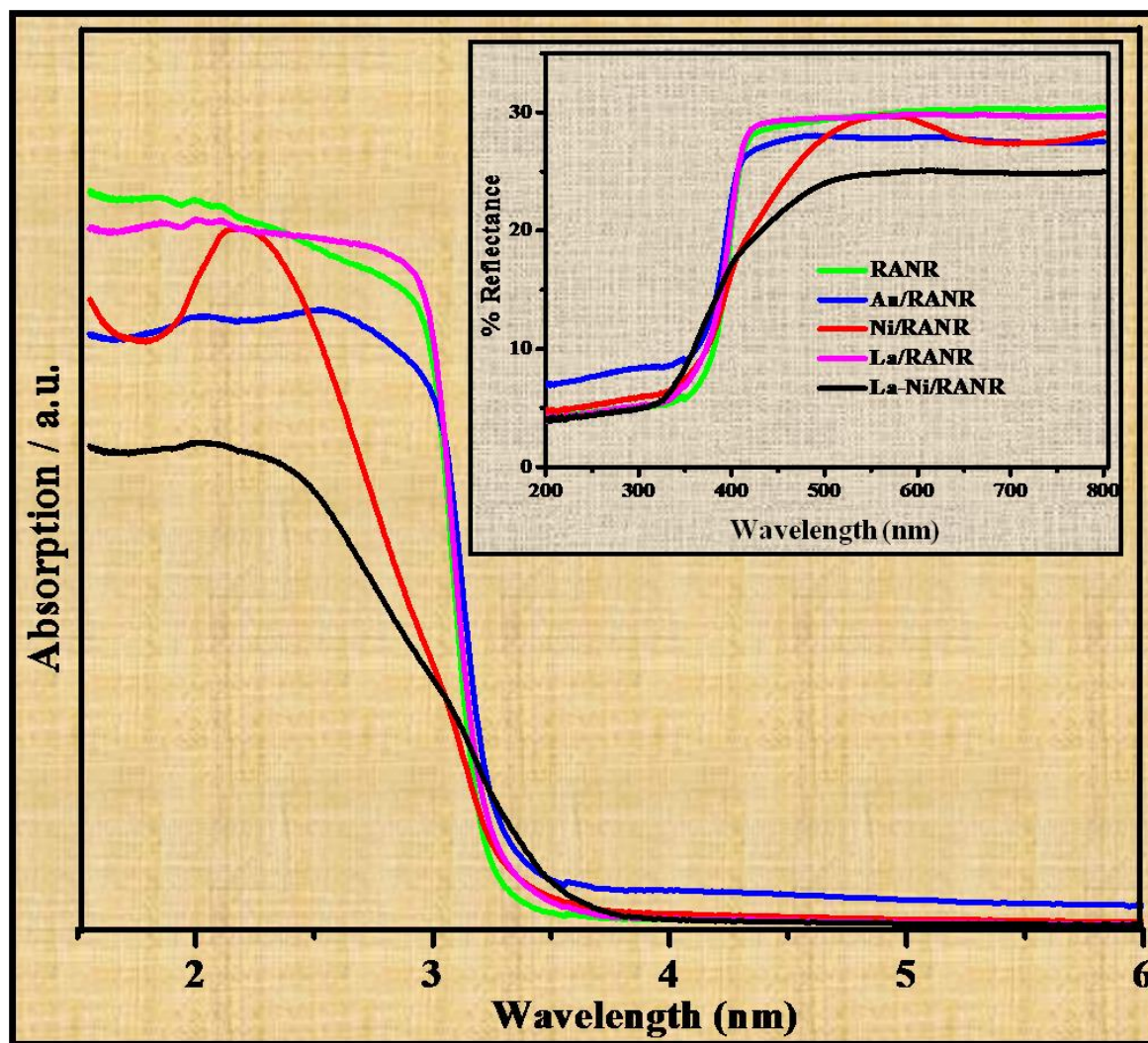


Figure 9.1 Diffuse reflectance UV-Vis spectra of supported Au, Ni, La, La-Ni/RANR and the Plain RANR photocatalysts.

The spectra in **Fig. 9.1** showed that the plain RANR have the highest wavelength response range to visible light region. Previous reports noted that La-doped TiO_2 has a stronger absorption in the visible region than the unloaded TiO_2 .²⁶ This is because La loaded TiO_2 has a tendency of increasing the wavelength response range. However, UV-vis DRS data presented in **Fig. 9.1** shows that the La/RANR had absorption spectrum less than that of plain RANR. It was also observed that there is no visible light extended absorption. This is attributed to the fact that the La particles are large and deposit on the TiO_2 surface and did not substitute Ti^{4+} in the TiO_2 lattice.^{7,27} This phenomenon is presented in **Fig. 9.1** with La/RANR showed a slight shift to visible-light region due to La-Ti interactions associated with charge compensation that may induce the generation of oxygen vacancies which may contribute to the observed slight shift to visible-light absorption. Ni approximates this

behaviour at a wavelength between 550 and 600 nm⁻¹. The Au and the co-loaded La-Ni/TiO₂ showed a decreasing wavelength response range respectively. **Fig. 9.1** also showed that the plain RANR, La/RANR and Au/RANR have no significant absorptions above 400 nm while La-Ni/RANR and Ni/RANR showed absorptions up to wavelengths of 500 and 650 nm respectively. A significant red shift of the DR spectra of the photocatalysts were observed and was due to absorptions between the activated metal catalysts and the rutile nanorods surfaces of the RANR.¹

9.4.2 Photoluminescence (PL) analysis

The photoluminescence spectral data gives a measure of the photocatalyst's efficiency to trap, transfer and separate charge carriers. The PL spectrum is generated from the electron-hole pairs transfer measured during the recombination tracking of the free charges.²⁸ The PL spectral analysis was carried out at the range 300–1000 nm. **Fig. 9.2** showed the major peak occurring around 420 nm within a 380 – 470 nm spectral range. The peak may be ascribed to emission due to incomplete surface passivation where radiationless recombination takes place.

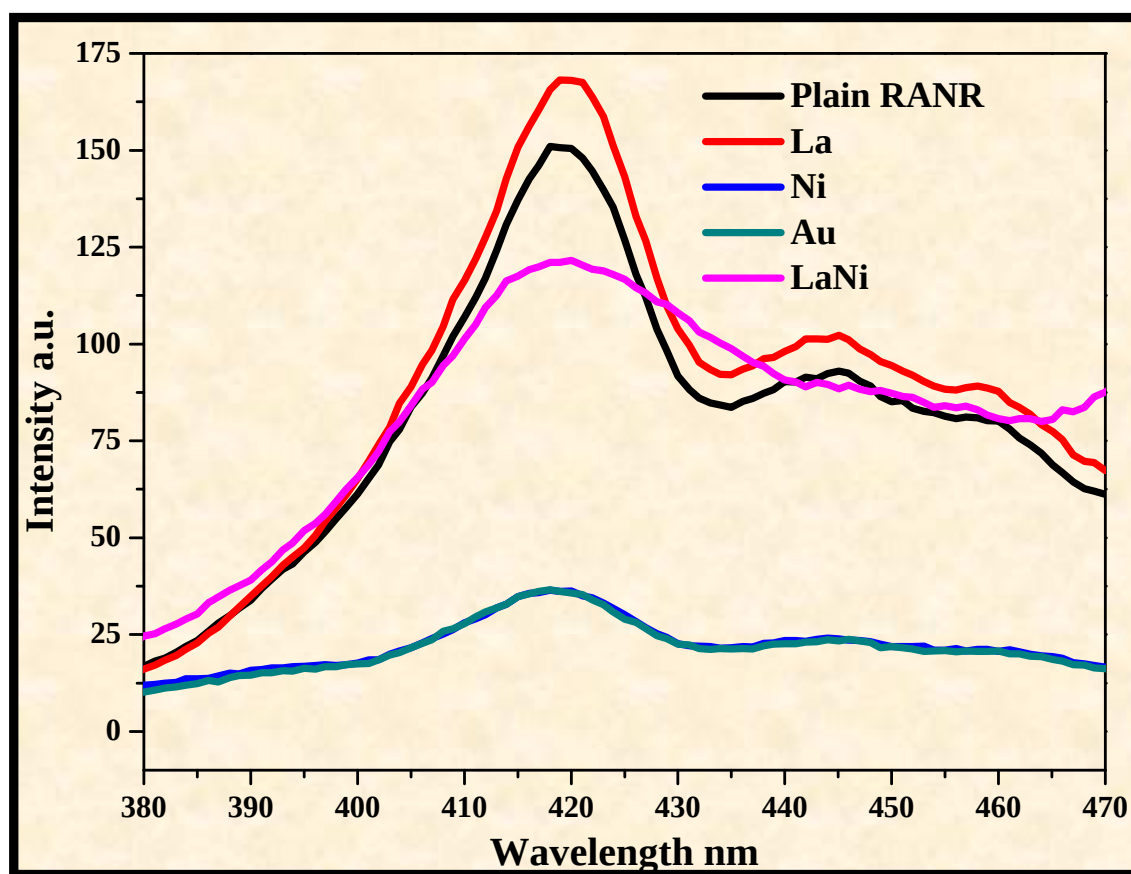


Figure 9.2 Photoluminescence spectra of the metal photocatalysts.

The plain RANR showed a broad PL emission band which is similar to that of La/RANR, though at higher intensity. However, the La-Ni/RANR showed a PL emission band that is broader than that of plain RANR suggesting that a new PL emission phenomenon had occurred. Previous studies observed Ni/TiO₂ exhibited a similar excitonic PL emission band to that of TiO₂.²³ However, **Fig. 9.2** showed narrower and low intensity PL emission band peaks of both Ni and Au/RANR catalysts. The latter also had a higher excitation wavelength of 400 nm in contrast to that of La, La-Ni and plain RANR which is 380 nm.

This implied that Ni and Au did not act as trapping sites to capture the photogenerated electrons from the conduction band of TiO₂ in their respective catalysts. The metals became the recombination centres of the e⁻/h⁺ pairs. Au, like La and La-Ni on the RANR surface, was expected to effectively act as a trapping site for the capturing of photogenerated e⁻/h⁺ pairs.^{23,29,30} But PL measurements suggested that Au and also Ni covered the active sites on the RANR thus decreasing the surface oxygen vacancy content and surface defect. Consequently, they become recombination sites. This explains the observed phenomenon in Section 9.4.1.1 with regard to extent of metal–RANR interactions that saw Ni and La exhibiting shifts to visible light absorption in UV–vis DRS analysis. Furthermore, the revelation of the fate of e⁻/h⁺ pairs in the respective supported catalysts augments the explanations behind their performance as catalysts in the synthesis of SCNMs of different morphologies, properties and characteristics as explained in **Chapters 5 – 8**.

9.4.3 Photodegradation rate studies

Preliminary reactions done using all the catalysts over the whole range of wt. % loadings revealed that the low wt. % loaded catalysts did not show significant photocatalytic activity (**Appendix E**). The observed results of low wt. % loading catalysts were similar to that of plain RANR in the photocatalytic degradation of MeO dye. This may be attributed to the low photo–quantum efficiency of the catalysts at low wt. % loading (< 5 wt. %). In this work, 5–8 wt. % loading was observed to be ideal for the photodegradation of MeO. At this wt. % loading range, the catalysts performed in a similar way. The photodegradation results were similar across this wt. % loading range. A representative wt. % loading of 8 wt. % was presented in this discussion. The catalysts with high metal wt. % loading (> 8), were characterised by high metal density on the support surface and hence reduced surface area and consequential lowered catalytic activity.

Fig. 9.3 is a plot of the change in concentration of the MeO per unit time. All the catalysts were maintained at 8 wt. % loading for control purpose. The photodegradation reactions were done under a fixed set of conditions in which a mass of 0.1g of catalyst was used to degrade a 50 mL of 50 ppm aqueous solution of methyl orange at the operating settings presented in **Section 9.3.1**. These conditions were maintained throughout the whole series of photodegradation experiments. **Fig. 9.5** presents the photodegradation rate of MeO and compared the photocatalytic performance of the supported catalysts under the set fixed conditions. It was observed that 8 wt. % La/RANR showed consistent high catalytic activity of all the supported catalysts. However, plain RANR exhibited better photocatalytic activity than all the supported catalysts, a phenomenon reported in many similar previous works. However, it was expected that supported catalysts would exhibit better photodegradation as reported in many previous studies. But in this work, Au and Ni/RANR catalysts did not perform as anticipated due to explanations presented in **Sections 9.4.1.1** and **9.4.1.2** respectively.^{3,6,7,23,30–36} **Fig. 9.3** showed a rapid MeO concentration decrease that depleted to zero at the end of the reaction catalysed by plain RANR. This implied that the plain RANR catalyst remained consistent and photocatalytically active with degradation efficiency that far exceeded that of Au, Ni, La and the co-loaded La-Ni/RANR catalysts.

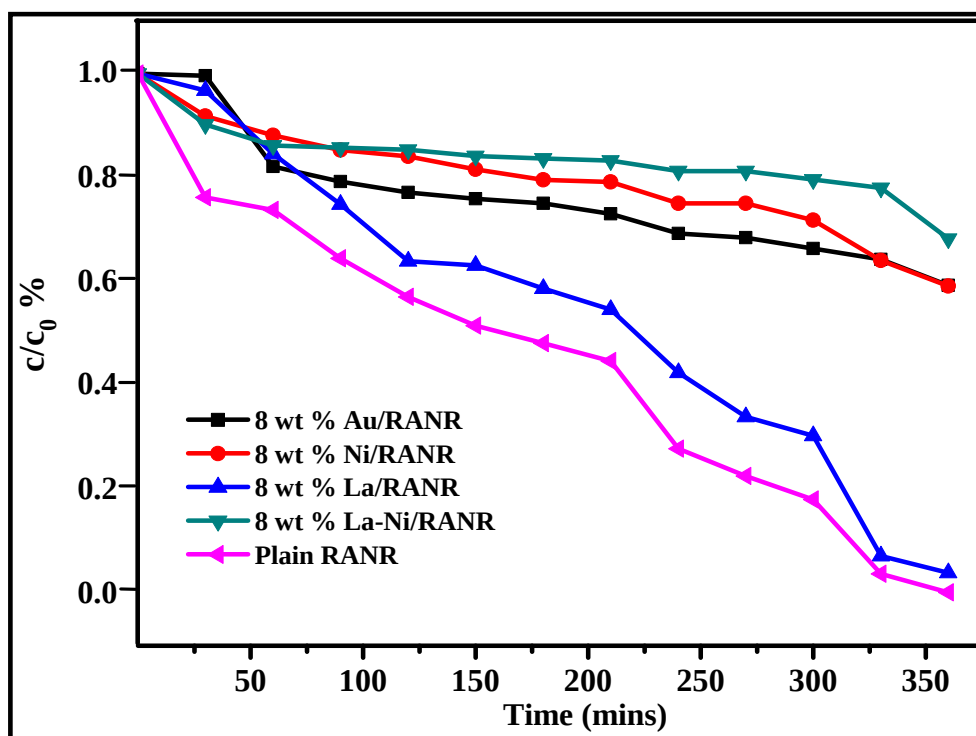


Figure 9.3 Photodegradation of MeO by 8% Au/RANR, Ni/RANR, La/RANR, La-Ni/RANR and plain RANR photocatalysts.

The performance of La/RANR may be explained in terms of the La inducing slightly higher Fermi level in the catalyst while promoting higher adsorptive affinity and a lower recombination rate than in other supported catalysts.³⁷ The photocatalytic activity of the Au and Ni/RANR was very low as degradation occurred up to only 40 % of the MeO in the solution while that of the La-Ni co-loaded catalyst is only 30 %, compared to 100 % degradation with the La/RANR and plain RANR photocatalyst in the 6 hour window that was monitored.

It was observed that although La/RANR catalyst exhibited high photocatalytic activity, there was notable poor performance of the co-loaded La-Ni/RANR. This implied that Ni actually inhibited the photocatalytic activity of both La and TiO₂ of the RANR structure due to reasons explained in **Sections 9.4.1.1** and **9.4.1.2**. The co-loaded La-Ni/RANR (**Chapter 8**) and the Ni/RANR (**Chapter 6**) were both observed to have a higher average particle size of around 5 nm as shown in **Section 4.4.2**. This rendered the active catalysts to be less optically absorbing. The metal species then supported e^-/h^+ pair recombination instead of being photogenerated electron trapping sites. The band – to – band transitions permit incomplete surface passivation and enable radiationless recombination to take place as observed and explained in **Section 9.4.1.2**. The catalysts then suffered less photon absorption capacity in the suspension and hence less effective in degrading the MeO in the solution³⁸ as shown in **Fig. 9.3**. It can be concluded that there was no positive synergistic effect on the photocatalytic and general catalytic activity of the co-loaded La-Ni/RANR catalyst. Therefore the RANR morphology with no active catalysts loaded on it is a better photocatalyst than all the supported catalysts.

9.5 Conclusion

The co-loaded La-Ni/RANR and the Ni/RANR were both observed to have a larger average particle size of around 5 nm and it was inferred that they became less optically absorbing and have recombination centres. The RANR and the supported catalysts exhibited a wide range of MeO degradation. The plain RANR showed the highest photocatalytic ability with the La/RANR closely resembling the behaviour of plain RANR. La induced higher Fermi levels in the catalyst and promoted higher adsorptive affinity and a lower recombination rate than in other supported catalysts, as proved by its photocatalytic behaviour relative to other supported catalysts. The photocatalytic activity of the Au and Ni/RANR was observed to be very low as the MeO degradation occurred up to only 40 % while that of the co-loaded La-Ni/RANR catalyst is only 30 %, compared to 100 % degradation with the La/RANR and plain RANR catalyst. The observed broad PL emission band showed that TiO_2 has a large band gap and the supported metals did not shift the TiO_2 absorption band and did not sufficiently foster the subdual of the electron-hole recombination. UV-Vis DRS analysis also showed that plain RANR has the highest wavelength response range to visible light region. There is no positive synergistic effect on the photocatalytic behaviour of the loaded metals and the RANR support in the catalysts.

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Chapter 10

General Conclusions and Future Studies

10.1 Conclusions

The work carried out in this research showed how RANR may be effectively used as a novel and alternative material to support nanosized metal particles to make supported catalysts. The RANR morphology provided a unique topology on which activated metal nanoparticles were supported. The preparation of the rutile phase RANR was observed to be of critical significance as both the rutile phase and the RANR morphology may not be easily attained under ordinary hydrothermal conditions. Detailed analyses revealed that various degrees of nucleation of rutile nanorods directly affected both the morphology of the RANR support structure and consequentially the topology of catalytic support. Structures ranging from scattered rutile nanorods, through different sizes of flakes of partially nucleated rutile nanorods to perfect spherical RANR structures were formed. This affected control over the deposition and support of the metal nanoparticles. Therefore a specific temperature (200 °C), coupled with an ideal TiCl_4 (12 mL) to water (100 mL) ratio gives perfect RANR spheres.

PXRD and EPMA provided preliminary data about the crystalline forms in which the supported catalysts exist. This helped establish the distribution of the phases in the catalyst material and stabilities of the respective phases. TPR measurements showed the reducibility of the catalyst materials from the calcined oxide forms of their preparation and reduction to metallic atoms with inherent catalytic properties and characteristics. TEM and SEM techniques showed the morphologies of the RANR and the RANR – supported catalysts, carbon materials and the data was used in size and diameters analysis and determinations. SEM micrographs showed the RANR spheres and the shapes of the CNFs while TEM data enabled extrapolation of the mechanism in which the materials formed from their constituent precursor materials.

DPU method was found to be an easy and viable approach for affording smallest particle size possible loaded on the RANR. It can be concluded that the mechanism of deposition required points of defects on the nanorods of the RANR on which the metal nanoparticles deposited after being precipitated out of the solution. It can be postulated that the activated metal nanoparticle ions selectively occupied positions of distortion of the Ti^{4+} cation site in the

lattice on the surface defect of the RANR. An acidic pH rendered the TiO_2 surface positively charged and prompted anionic precursor metals to electrostatically attach on the RANR support. It was conclusively observed that the points of defects accessible for metal nanoparticles deposition were only those around the tips of the rutile nanorods of the RANR structure. Thus the sections of the nanorods enclosed within the RANR remained sterically hindered and inaccessible. These explanations and interpretations addressed the primary aims of the research to prepare the RANR and loading the Au, Ni, La and co-loaded La-Ni metal nanoparticles, and carrying out detailed analyses to determine particle sizes, crystallographic properties, and effect of reaction conditions on the success of the prepared materials as catalysts.

Parametric studies done on the method of preparation of the supported catalysts revealed detailed information at different wt. % metal loading. Metal nanoparticle size distribution, effect of wt. % loading, and surface area was explained. It may be concluded that particle size is a function of the progress of hydrothermal decomposition of urea. The reaction pH increased with urea decomposition and this supported the surface charge density of the precursor metal anion to be altered. Consequentially, the precursor metal particles went through enhanced disintegration and hence broke down into smallest particle size possible.

Performance studies on the respective supported catalysts were done parametrically using a CVD method of synthesis of SCNMs. Parameters varied were metal catalyst used, temperature, time, wt. % metal loading and gas flow rate. La/RANR catalysts synthesized simple CNFs while Ni/RANR catalysed the synthesis of twisted CNFs. Long chain straight-chain CNFs were synthesized over Au/RANR while a mixture of both straight and twisted CNFs were synthesized over the co-loaded La-Ni/RANR catalysts. La/RANR did not catalyse the synthesis of SCNMs at lower wt. % metal loadings < 5 wt. %. This is assumed to be due to La assimilating TiO_2 in its chemical properties, characteristics and photochemistry. It is at higher composition that La assumed its distinguishable catalytic properties and facilitated the synthesis of simple CNFs. The ideal composition is 8 wt. % which exhibited well dispersion with excellent spatial distribution and very low particle size range. However, Ni/RANR catalysts had Ni nanoparticles sparsely dispersed in a more homogeneous particle size distribution, and maintained a small particle size range even at higher wt. % loading. High temperatures and metal wt. % loading supported growth of CNFs with increased graphiticity and longer carbon chains while the Ni catalysts characteristically shaped the carbon materials into their specific twisted morphology.

The DPU method also afforded monodispersion of the Au catalysts nanoparticles on the RANR support. The particles tended to systematically increase in size with increase in wt. % loading. Therefore wt. % loading could be used to control particle size distribution of the AuNPs. Although Au deposition from 0.25 – 10 wt. % was achieved, it was observed that none or very little CNFs form at low wt. % loading. La-Ni/RANR co-loaded catalysts presented a different set of phenomenon as compared to the monocatalysts. The co-loaded metal nanoparticles supported the synthesis of a mixture of long straight chain CNFs and twisted CNFs via a CVD method.

Detailed studies revealed that there was no significant intrinsic synergistic effect observed in the La-Ni/RANR co-loaded catalysts performance during the CVD synthesis of CNFs. Each metal on one end of the La-Ni particle catalysed fibres of different morphologies with straight chain and twisted CNFs at La and Ni ends respectively. The reaction parametric conditions affected the syntheses involving all the different types of catalysts in a more or less similar manner. The parameters influenced the quality, properties, characteristics, and yield of the CNFs synthesized. The various characterisation techniques unravelled detailed evidence on how varying reaction condition parameters influenced the CVD synthesis of SCNMs.

LRS was also used in the characterisation of carbon and catalysts materials with their vibrational frequencies giving an intrinsic understanding of their crystallographic forms and atom–atom interactions. The Raman data is complemented by TGA analysis by way of performing high precision measurements of weight loss or gain with temperature. This information points to the degree of crystallinity in the carbon material while it shows species atomic interactions and bonding in inorganic materials. These characterisations were used to explain the trends in the systematic variation in each parameter. However all parameters showed a common trend in which a quality or quantity had a threshold range of conditions over which it is well exhibited with the other extremes exhibiting undesirable characteristics. A further application of the supported catalysts was done by testing their photocatalytic performance in the photodegradation of MeO. The support material showed exceptional photocatalytic performance than all the supported catalysts. La/RANR closely resembled RANR in its performance. This was attributed to induced higher Fermi levels that promoted La higher adsorptive affinity and a lower recombination rate than in other supported catalysts.

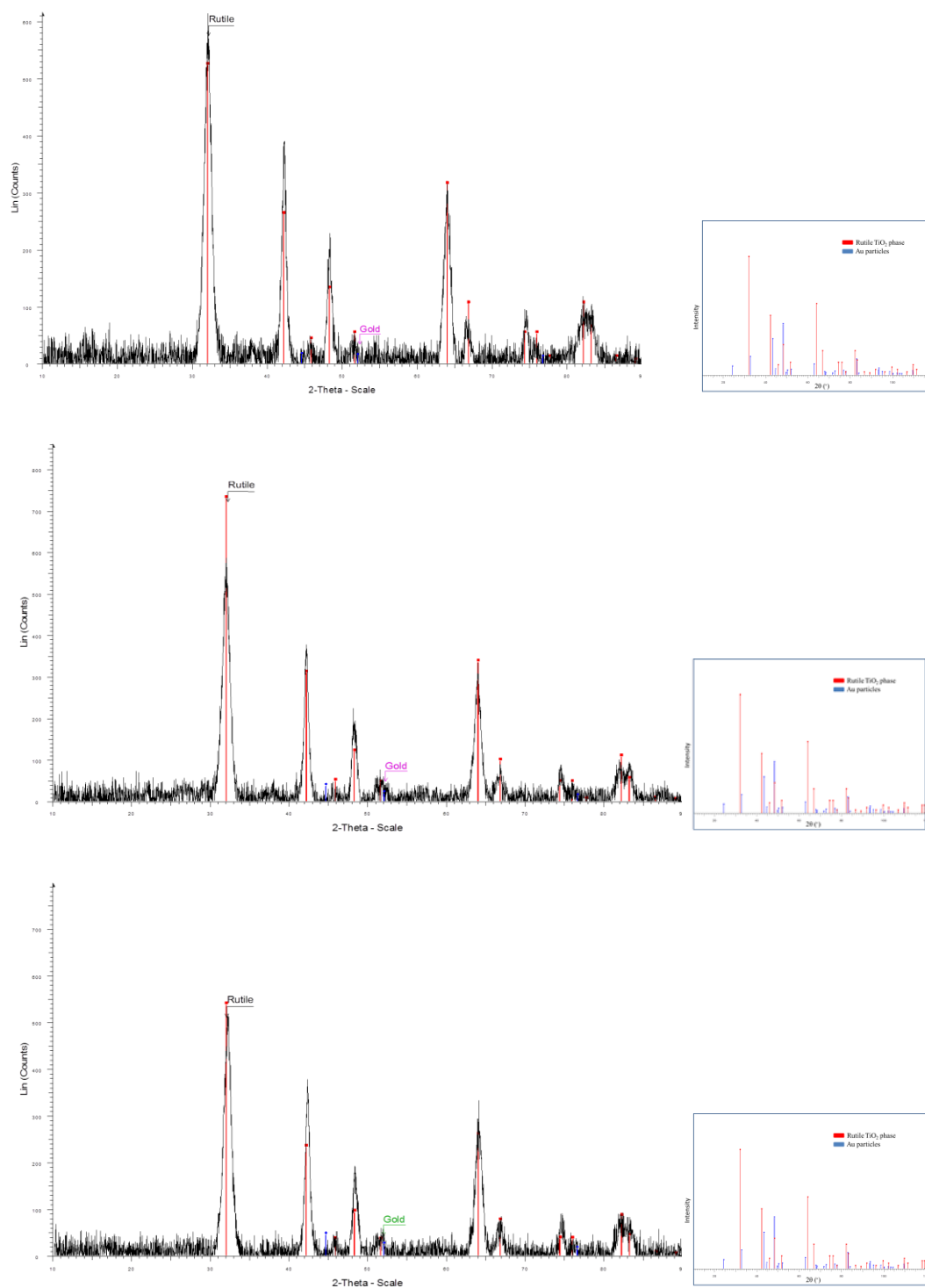
10.2 Future Research

This research work presented a novel alternative way of using TiO_2 as a support material other than the ordinary anatase and rutile morphologies. The RANR have proved to present a unique topology over which nanosized metal catalyst particles may be supported. However, a lot of aspects remained unaddressed such that future work would need to further investigate the following ideas.

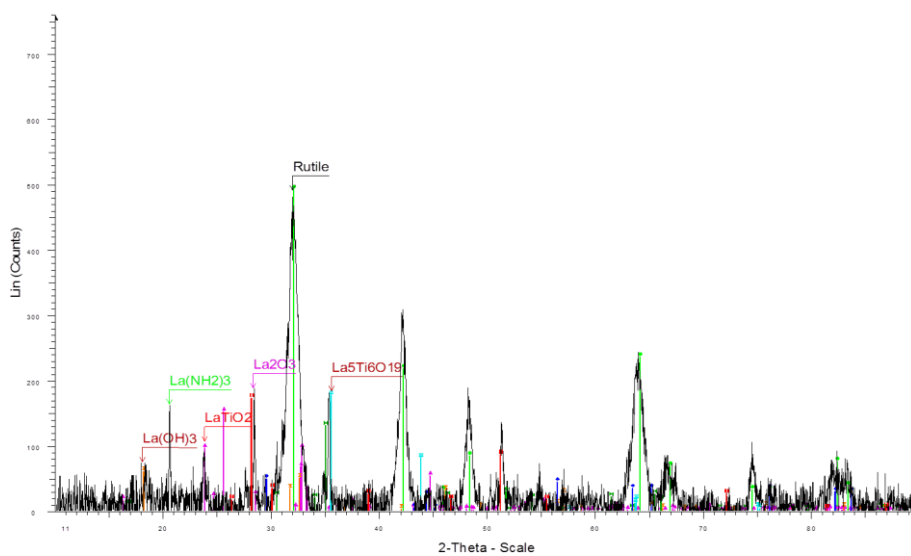
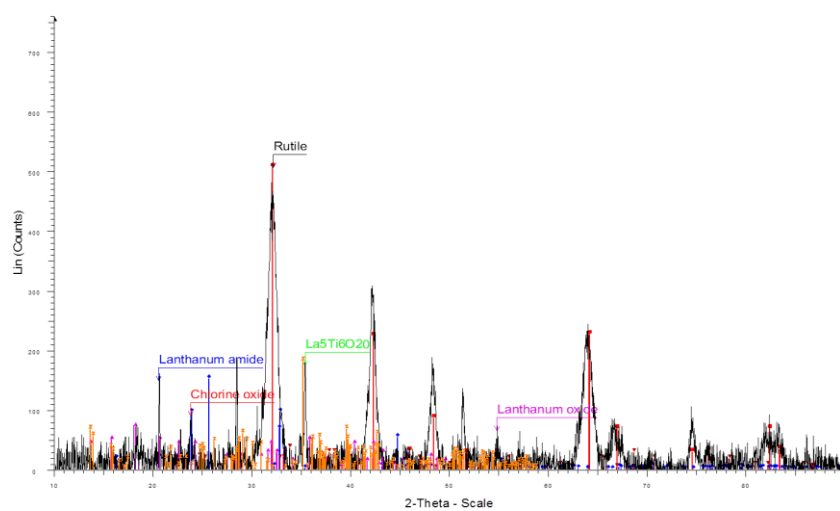
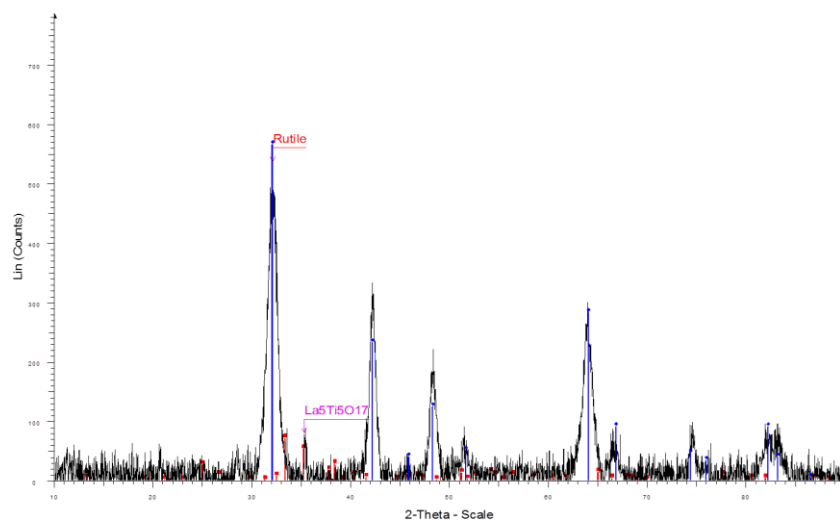
- Kinetic studies on the mechanism of nanorod growth to account for the development and types of surface defects on the RANR.
- Exploring the mechanism of nucleation of the rutile TiO_2 nanorods during RANR morphology formation.
- Carry out kinetic studies to try and obtain perfect RANR from bulk synthesis of RANR.
- Explore ways of improving and increasing the surface area of the RANR.
- Carry out detailed studies on the surface–surface interaction of the RANR support and the metal nanoparticles by establishing the nature and strength of chemical interactions at the metal–support interface.
- Attempt to manipulate the surface properties of the RANR in an effort to control particle sizes of the deposited metal nanoparticles.
- Explore alternative mechanisms of carbon nanomaterials growth other than the tip–growth mechanism to prevent sintering of metal nanoparticles and consequential increased thickness of the fibres synthesized.
- Carry out more parametric control experiments that target the synthesis of single-walled carbon nanotubes SWCNTs or few-layered and multi-walled carbon nanotubes MWCNTs.
- Explore possibilities of making electrochemical cells using RANR–catalyst–CNFs network.
- Attempt manipulating growth mechanism to make very long carbon nanotubes or fibres for use in making aircraft bodies and other high performance equipment.

Appendix A

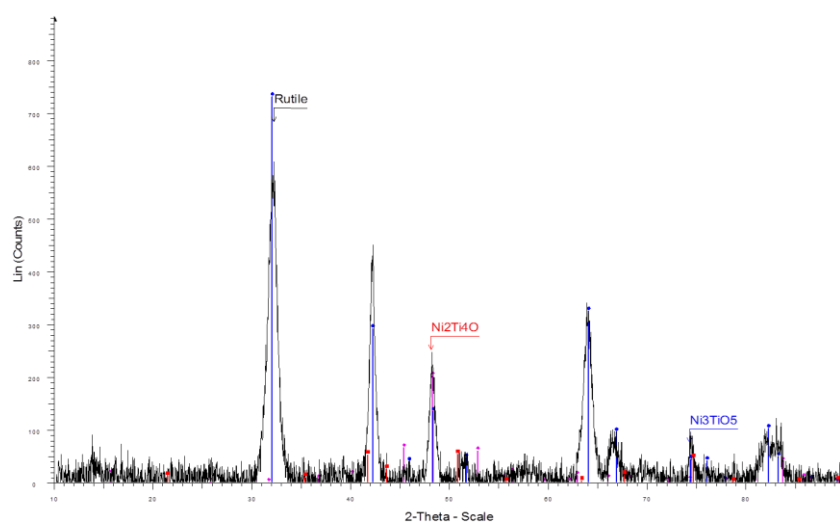
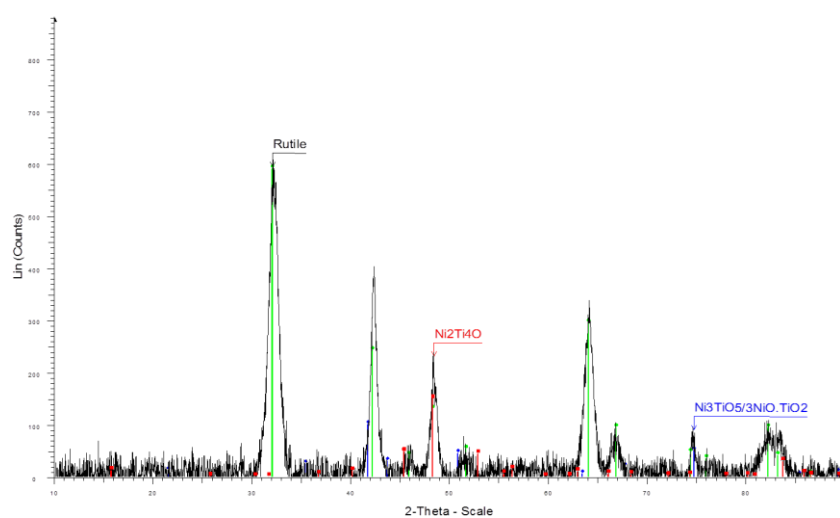
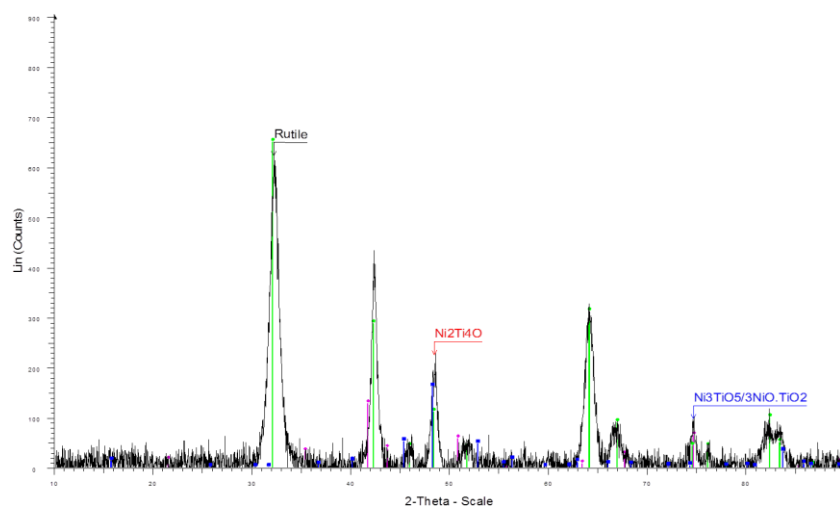
The crystallographic forms of the prepared supported catalysts are presented in the respective PXRD patterns and complemented with the associated EPMA plots.



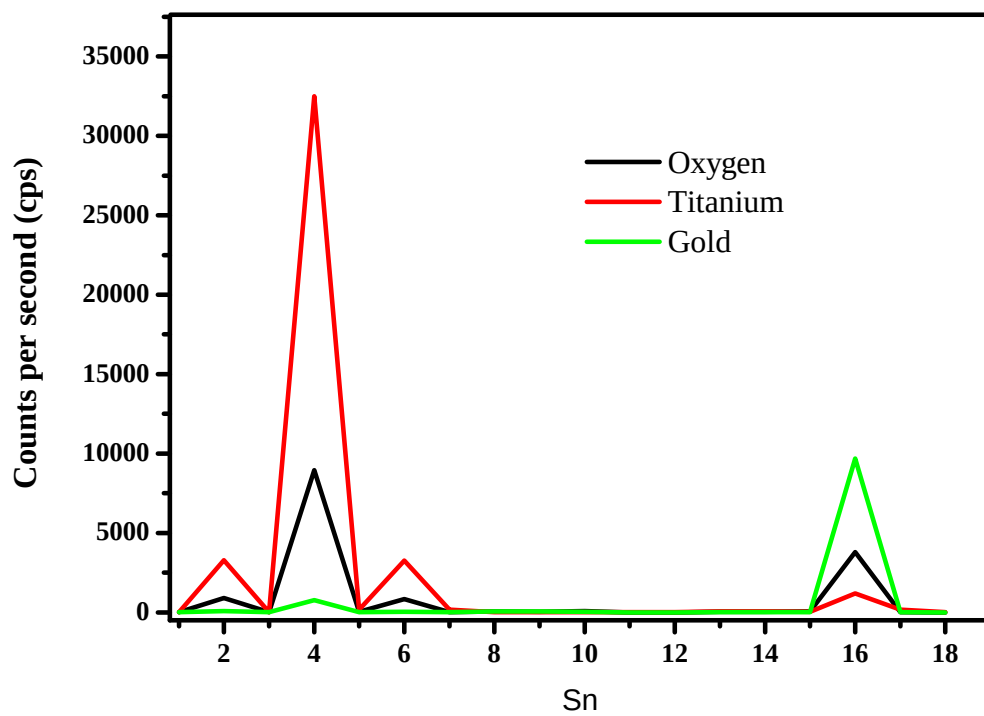
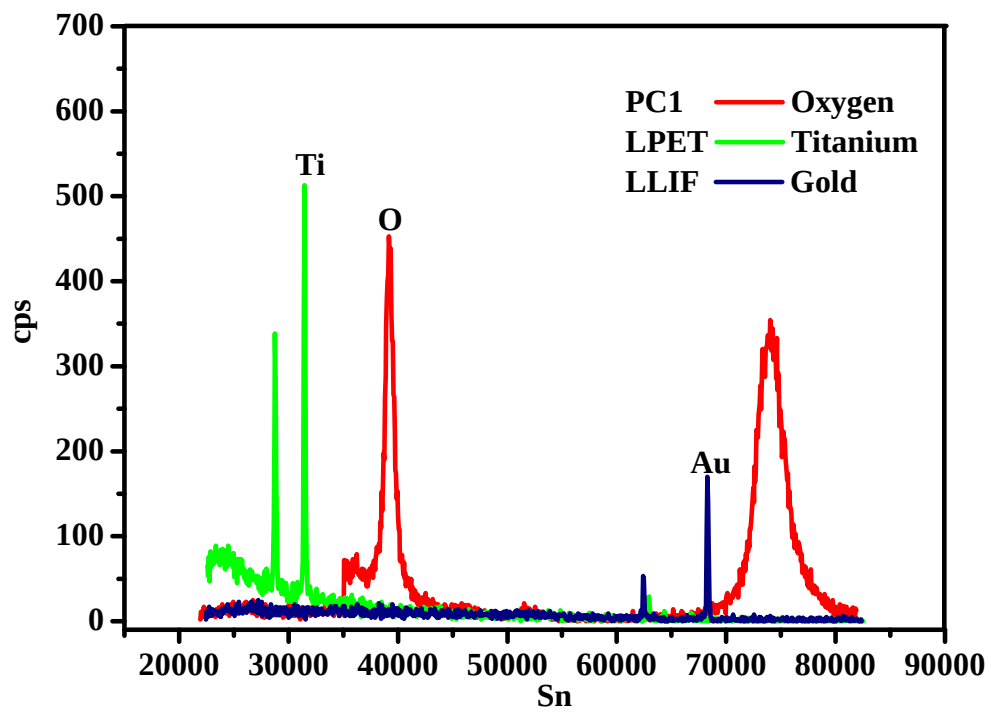
PXRD patterns of supported Au/RANR catalysts at 5 wt. %, 8 wt. % and 10 wt. % respectively. Samples were prepared under same DPU conditions and calcined at 500 °C for 1 hr.

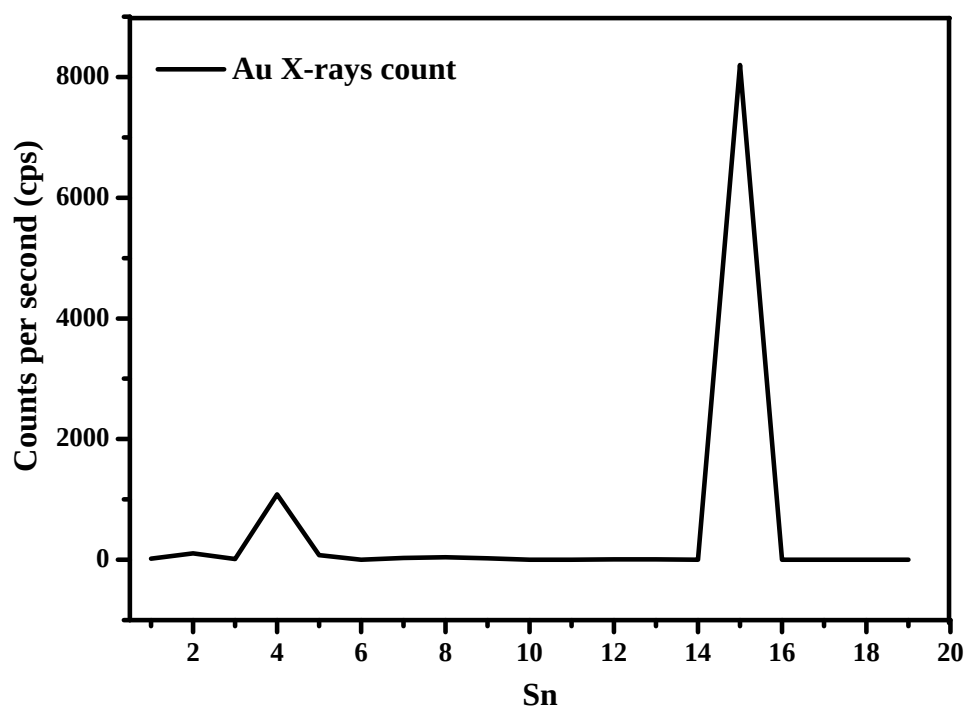


PXRD patterns of supported La/RANR catalysts at 5 wt. %, 8 wt. % and 10 wt. % respectively. Samples were prepared under same DPU conditions and calcined at 500 °C for 1 hr.



PXRD patterns of supported Ni/RANR catalysts at 5 wt. %, 8 wt. % and 10 wt. % respectively. Samples were prepared under same DPU conditions and calcined at 500 °C for 1 hr.





EPMA patterns of supported Au/RANR catalyst at 10 wt. % prepared by DPU and calcined at 500 °C for 1 hr.

Generation of EPMA data in quantification of the elements occurring in the supported catalysts was carried out under a set of analysis parameters and conditions. Below is an example of the analysis conditions settings for the quantification of 8 wt. % Au/RANR. Similar settings were put up in the analysis of the La, Ni and LaNi supported catalysts at different weight percentage compositions.

FileName : 8 wt. % Au-TiO₂ quantification 04.11.2015.qtiDat

Signal(s) Used : O Ka, Ti Ka, Au La

Spectrometers Conditions : Sp2 PC0, Sp5 LLIF, Sp3 LLIF

Full Spectrometers Conditions : Sp2 PC0(2d= 47.033,K= 0.00238), Sp5 LLIF(2d= 4.0267,K= 0.000058), Sp3 LLIF(2d= 4.0267,K= 0.000058)

Column Conditions : Cond 1 : 15keV -0.001nA

Date : 4-Nov-2015

User Name : SX

Setup Name : 8 wt. % Au-TiO₂ QUANTIFICATION 04.11.2015.qtiSet

DataSet Comment :

Comment :

Analysis Date : 11/4/2015 10:03:04 AM

Project Name : Default Project

Sample Name : Default Sample

Analysis Parameters :

Sp	Elements Blin Wind	Xtal Mode	Position	Bg+	Bg-	Slope	Bias	Gain	Dtime
Sp2	O Ka Inte	PC0	50315	-2000	2000		1450	555	3 560
Sp5	Ti Ka Inte	LLIF	68247	-600	600		1820	374	3 560
Sp3	Au La Inte	LLIF	31675	-600	600		1820	309	3 560

Peak Position : Sp2 50315 (-2000, 2000), Sp5 68247 (-600, 600), Sp3 31675 (-600, 600)

Current Sample Position : X = 14514 Y = 358 S = 287

Standard Name :

O On Albite

Ti On Rutile

Au On Au

Standard composition :

Albite = Na : 8.662%, Al : 10.46%, Si : 32.14%, O : 49.03%, K : 0.14%, Ca : 0.16%

Rutile = O : 40.06%, Ti : 59.94%

Au = Au : 100.0%

Calibration file name (Element intensity cps/nA) :

O : Albite_O Sp1_O Sp2_001.calDat (O : 120.7 cps/nA)

Ti : Rutile_TiSp3_TiSp5_001.calDat (Ti : 175.8 cps/nA)

Au : Au_AuSp3_AuSp5_001.calDat (Au : 86.3 cps/nA)

Beam Size : 0 μ m

	Beam curr (nA)		Peak cnt (cps)		Peak Time (s)	Peak (cts)		Ix (c/s/nA)		Pk-
Bg (cps)	Pk/Bg		Bg cnt (cps)	Bg1 cnt (cps)		Bg2 cnt (cps)		Ix/Istd	Ix/Ipure	
	Weight%		Norm Weight%		Atomic%		Det.Lim ppm		StdDev	wt% S
	A	F								
	1 / 1 .									
O	21.82	652.00	10.00	6506.00		28.80	628.40	27.62	23.60	23.60 23.60
	0.24	0.06	34.69	36.11	63.52	4339.	1.47	0.01	10.30	1.00
Ti	21.82	3800.37		10.00	37533.00		173.05	3775.37		152.00 25.00
	25.20	24.80	0.98	0.53	59.08	61.49	36.13	1266.	3.86	0.48 1.03
	1.00									
Au	21.82	66.81	10.00	668.00	1.27	27.81	1.71	39.01	37.80	40.21 0.01
	0.01	2.31	2.41	0.34	8387.	0.82	0.14	1.01	1.00	
Total										
	96.08	100.00	100.00							

EPMA analysis of the La-Ni/RANR mixed-metal catalyst.

FileName : 10 wt. % LaNi-TiO₂ spectra 26-01-16.wdsDat (Current dataset : 1)

Signal(s) Used : Sp1, Sp2, Sp3, Sp5

Spectrometers Conditions : Sp1 PET, Sp2 PC0, Sp3 LLIF, Sp5 LLIF

Full Spectrometers Conditions : Sp1 PET(2d= 8.75,K= 0.000144), Sp2 PC0(2d= 47.033,K= 0.00238), Sp3 LLIF(2d= 4.0267,K= 0.000058), Sp5 LLIF(2d= 4.0267,K= 0.000058)

Column Conditions : Cond 1 : 15keV 20.0857nA

Date : 27-Jan-2016

User Name : SX

Setup Name : 10 wt. % LaNi-TiO₂ spectra.wdsSet

DataSet Comment :

Comment :

Analysis Date : 1/26/2016 1:33:07 PM

Project Name : Default Project

Sample Name : Default Sample

Analysis Parameters :

Sp	Xtal	Bias	Gain	Dtime	Blin	Wind	Mode
Sp1	PET	1300	1012	3	560		Inte
Sp2	PC0	1486	524	3	560		Inte
Sp3	LLIF	1820	374	3	560		Inte
Sp5	LLIF	1823	426	3	560		Inte

Peak Position : Sp1 22014, Sp2 21864, Sp3 22539, Sp5 22417

Stage Position : X = 18912 Y = 1087 S = 82

Wds Spectrometers Starting position : 22044, 21894, 22569, 22447

Step Numbers : 1000 Channel

Wds Spectrometers Step size : 60, 60, 60, 60

Dwell Time : 1.5 Sec

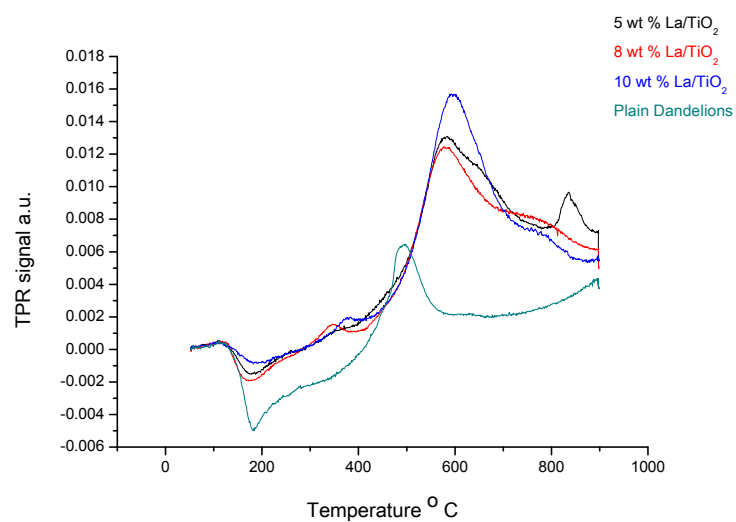
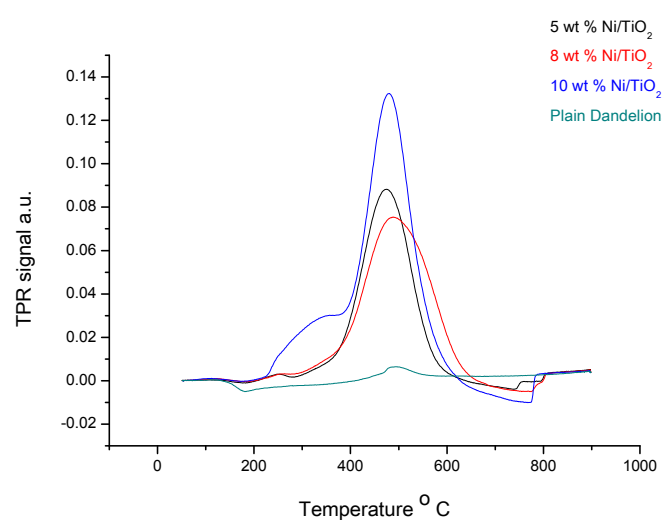
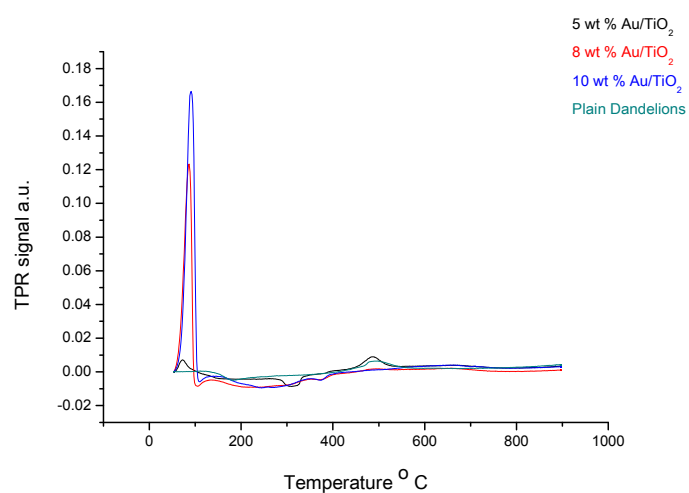
Beam Size : 0 μm

X Unit : Sinus-Theta

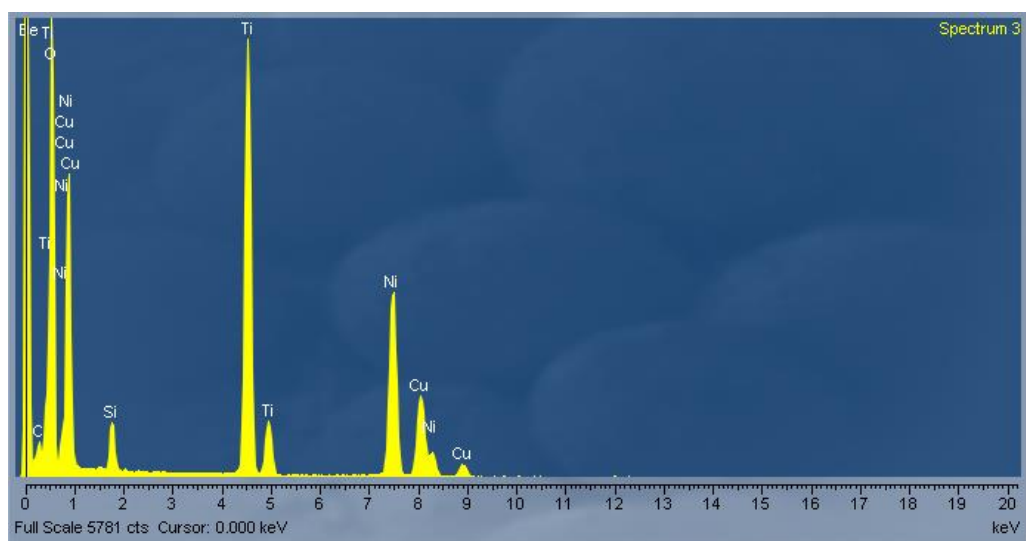
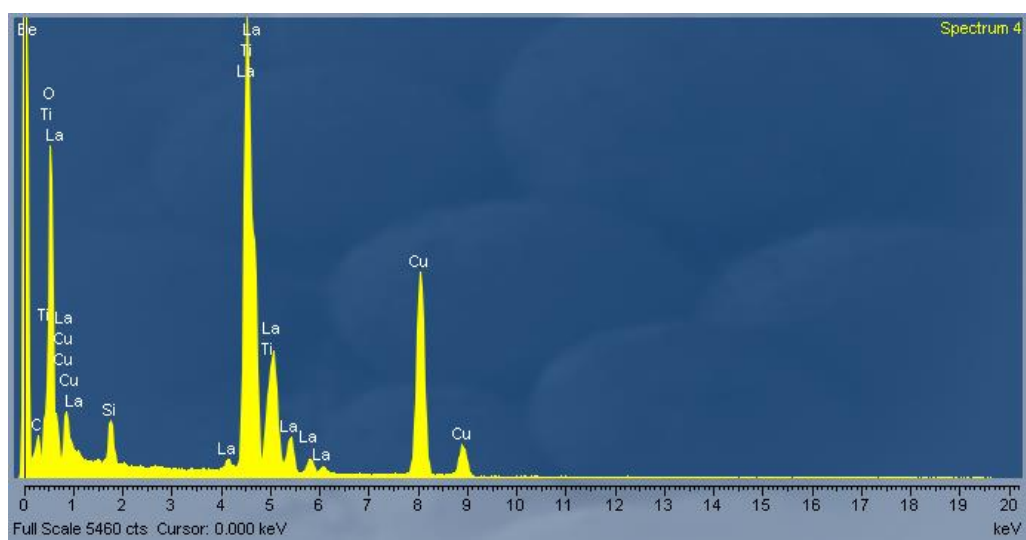
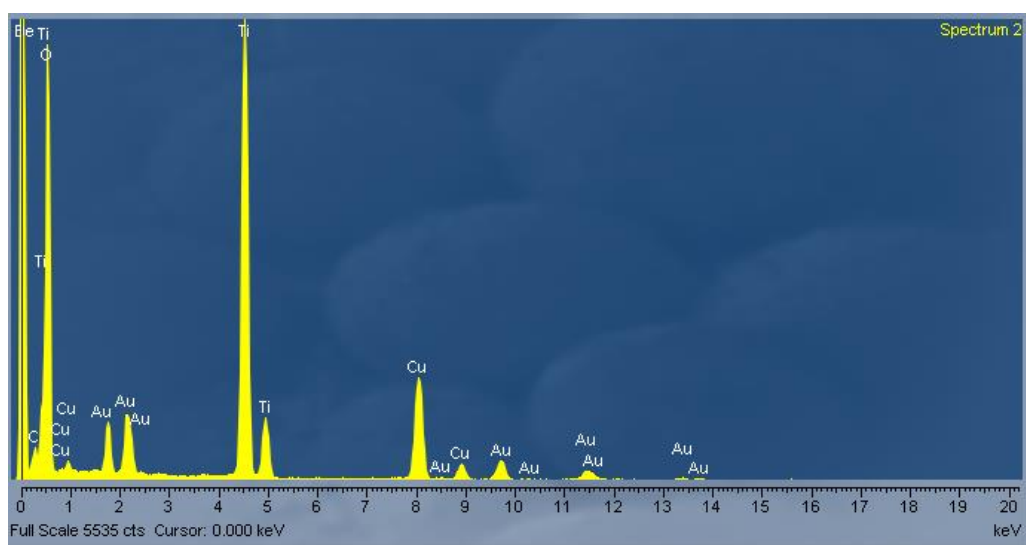
Y Unit : counts/sec

Pos	PET	Pos	PC0	Pos	LLIF	Pos	LLIF
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22447.00000	24.00075						
22104.00000	46.00698			21954.00000	420.58290	22629.00000	13.33392
	22507.00000	24.66746					
22164.00000	48.00760			22014.00000	330.35980	22689.00000	8.66692
	22567.00000	18.00042					
22224.00000	38.00476			22074.00000	259.55550	22749.00000	13.33392
	22627.00000	14.00025					
22284.00000	28.00259			22134.00000	189.45170	22809.00000	10.00033
	22687.00000	14.66695					

TPR analysis of the supported catalysts.



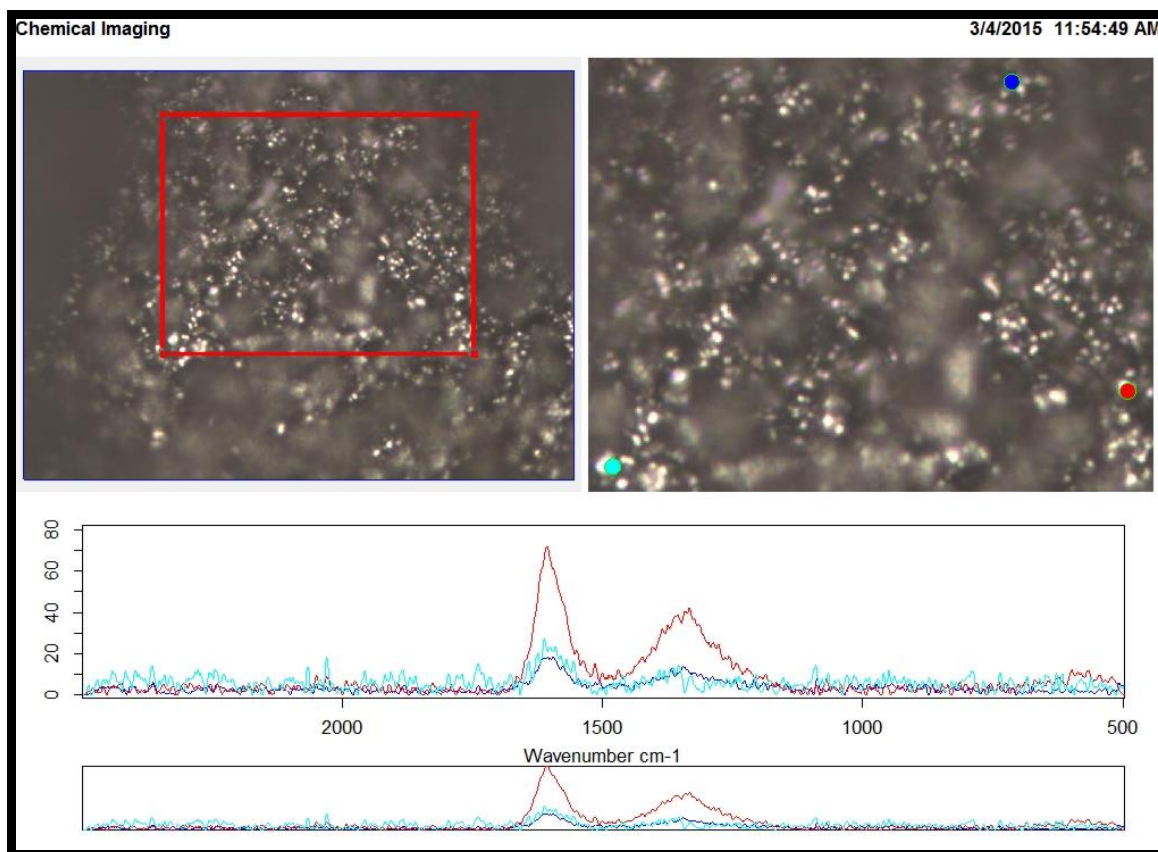
TPR profiles of the supported Au, Ni and La catalysts at 5 wt. %, 8 wt. % and 10 wt. % respectively compared against plain RANR. Samples were prepared under same DPU conditions and calcined at 500 °C for 1 hr.

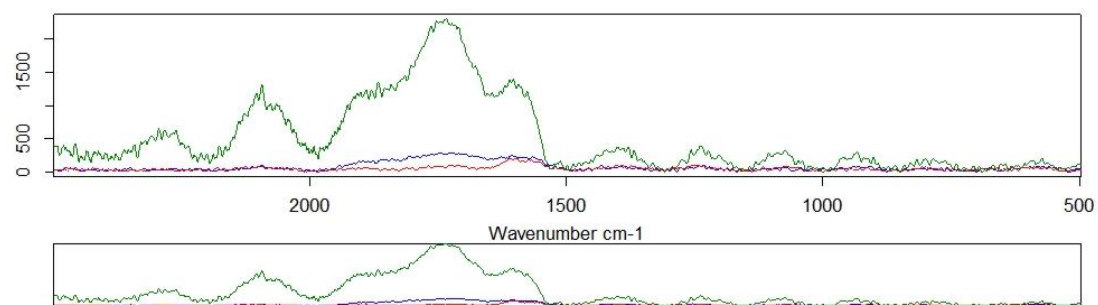
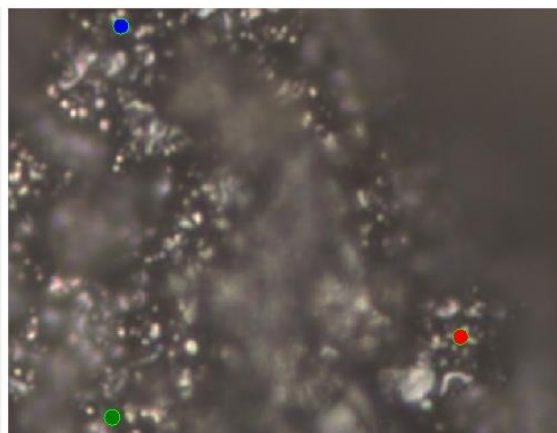
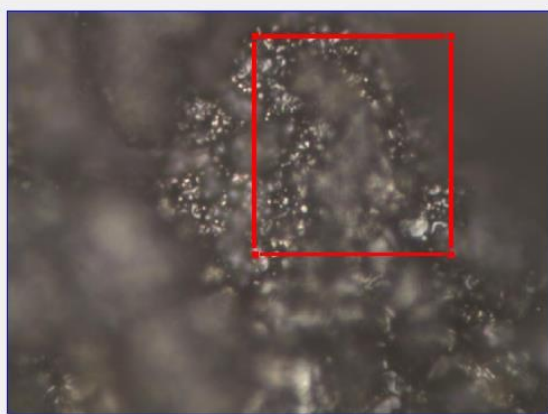
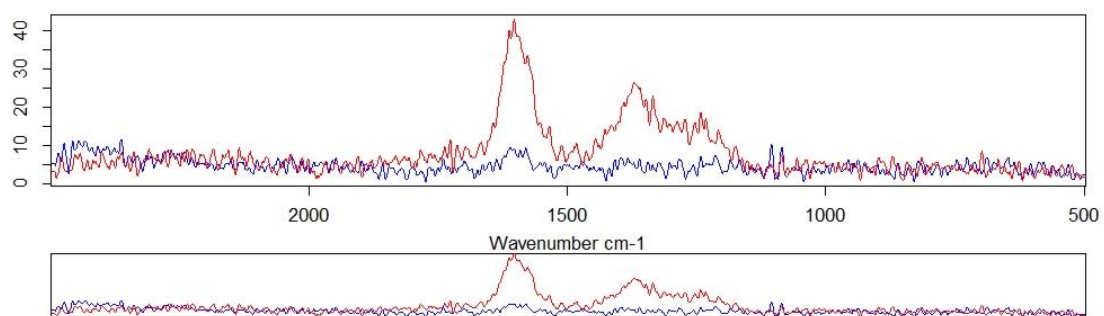
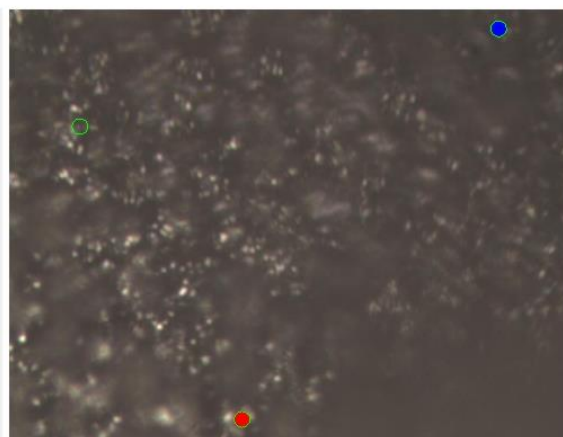
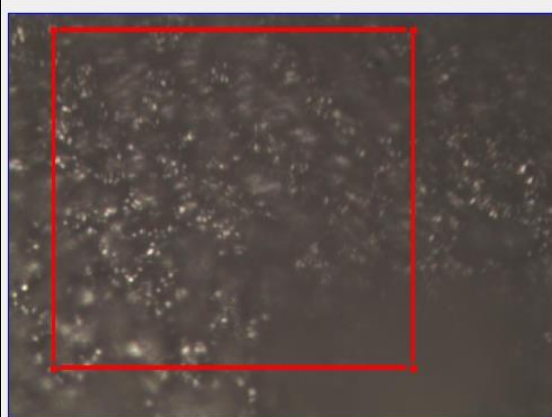


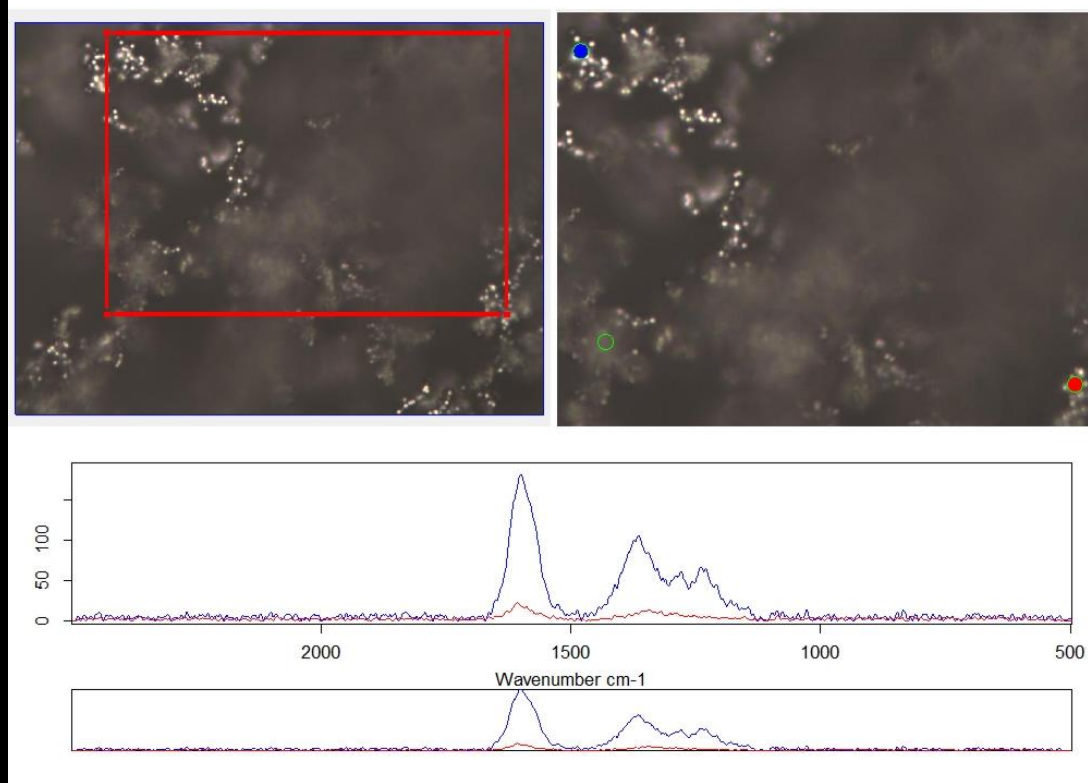
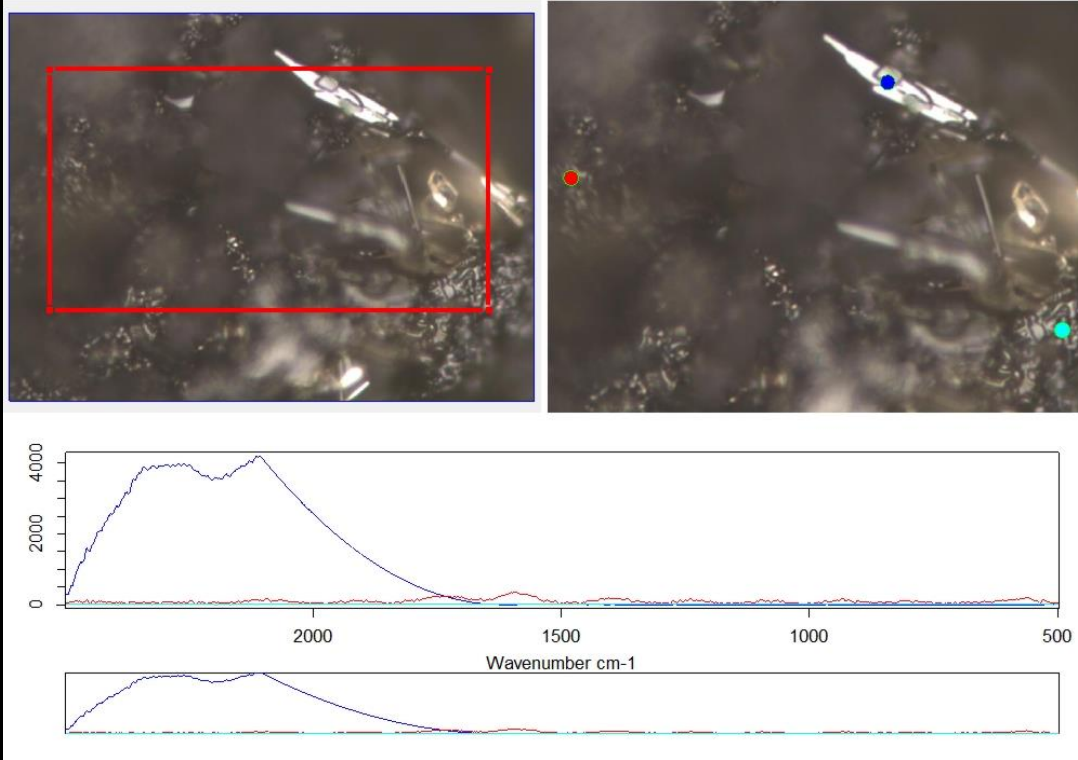
EDS profiles of the supported 10 wt. % Au, La and Ni catalysts calcined at 500 °C for 1 hr.

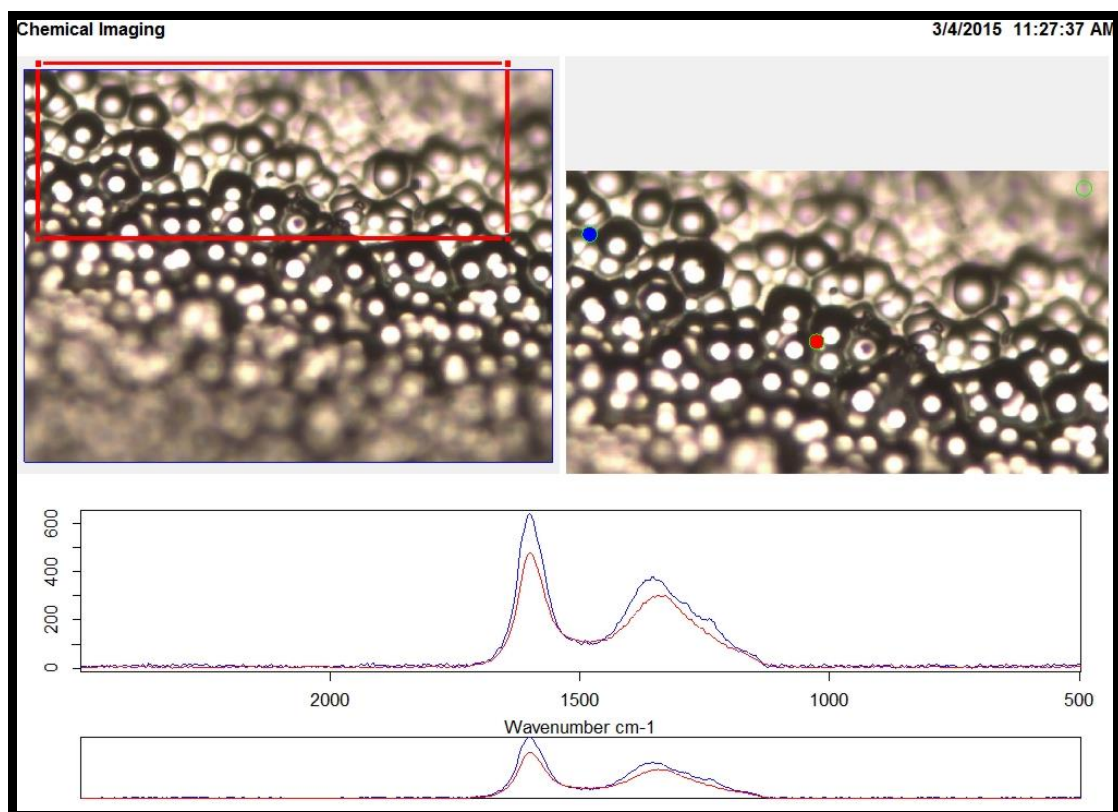
Appendix B

Supplementary data of the Raman analyses of the as-synthesized SCNMs on their respective supported catalysts.

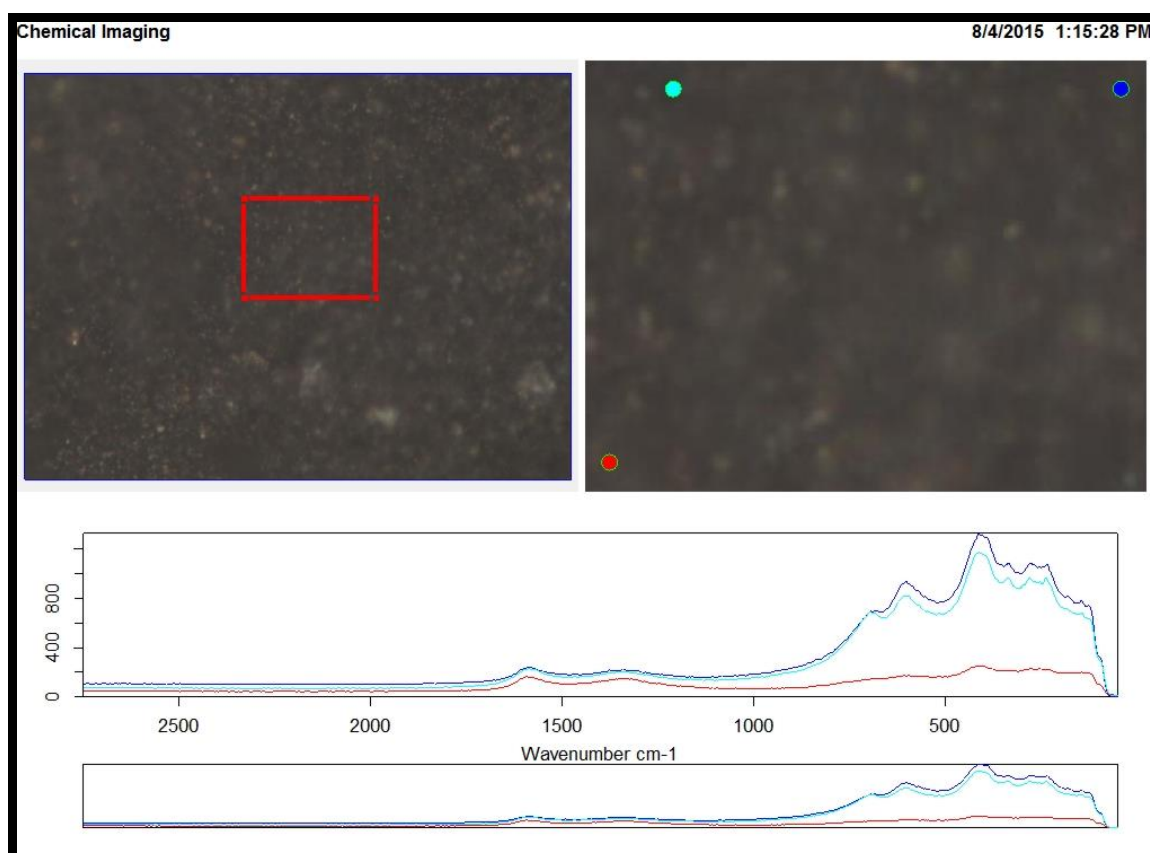




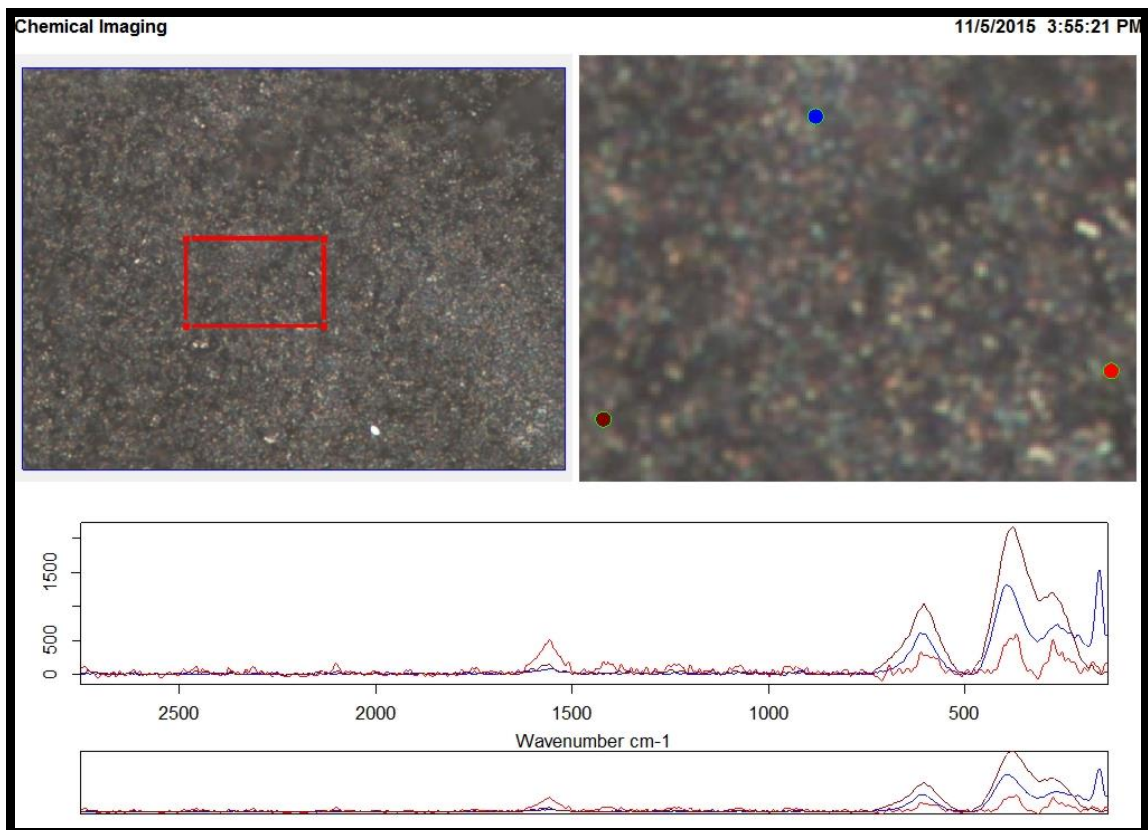
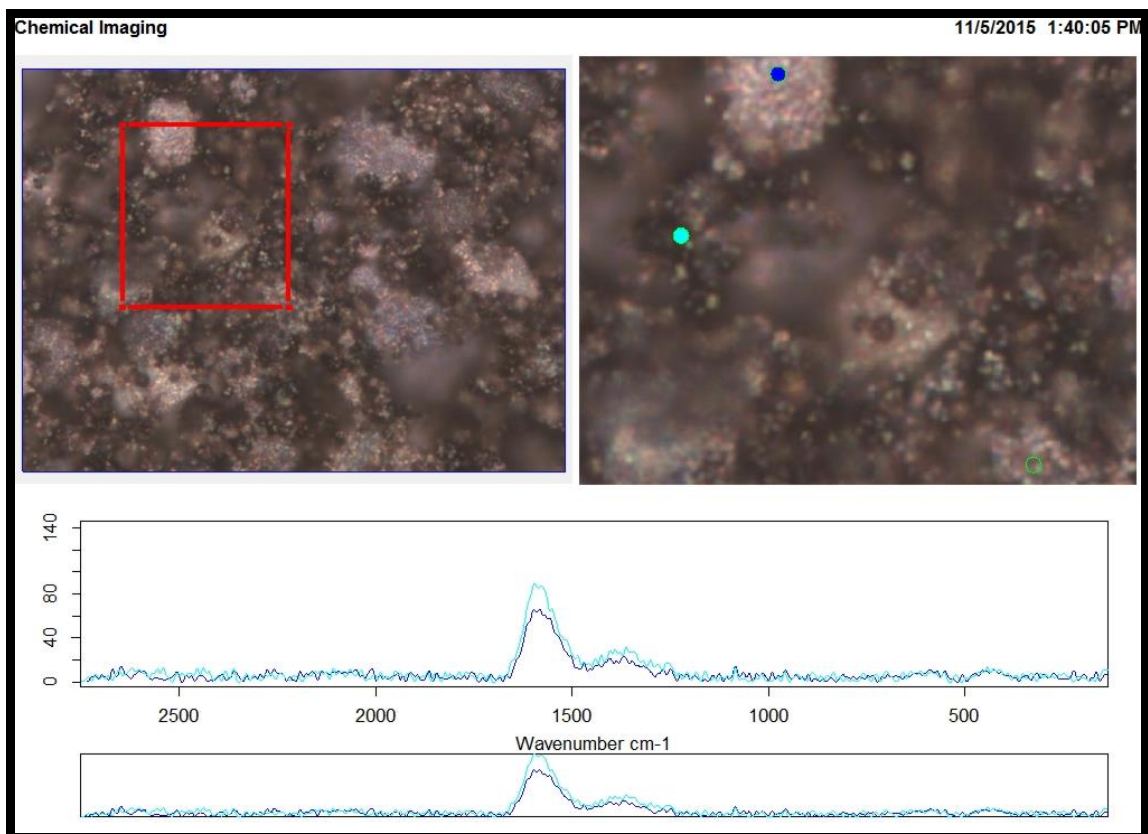




Raman maps and 3 – point spectral scans of CNFs synthesized over La/RANR at 700 °C.



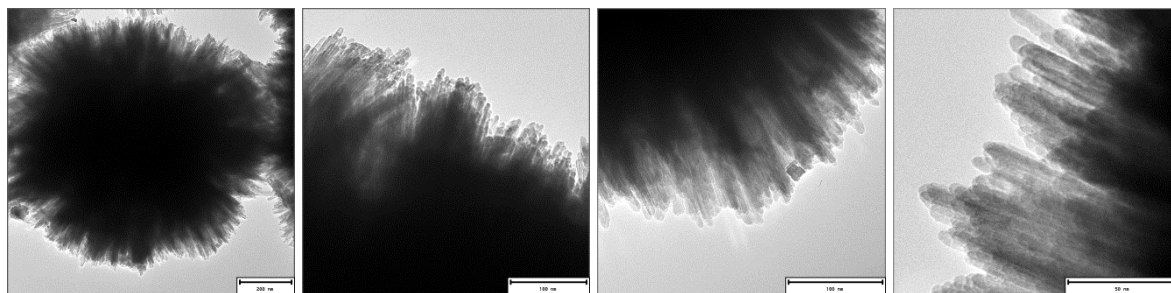
Raman maps and 3 – point spectral scans of CNFs synthesized over Ni/RANR at 300-700 °C



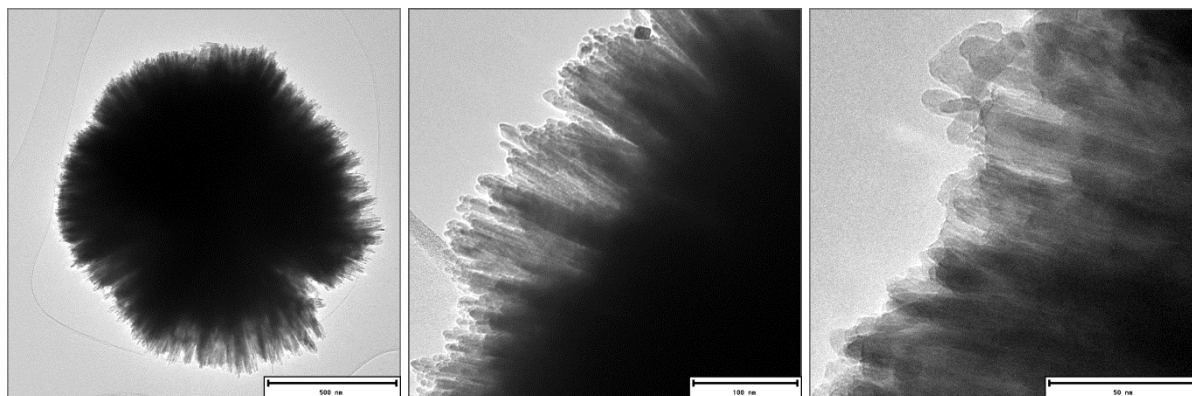
Raman maps and 3 – point spectral scans of CNFs synthesized over Ni/RANR at 300-500 °C.

Appendix C

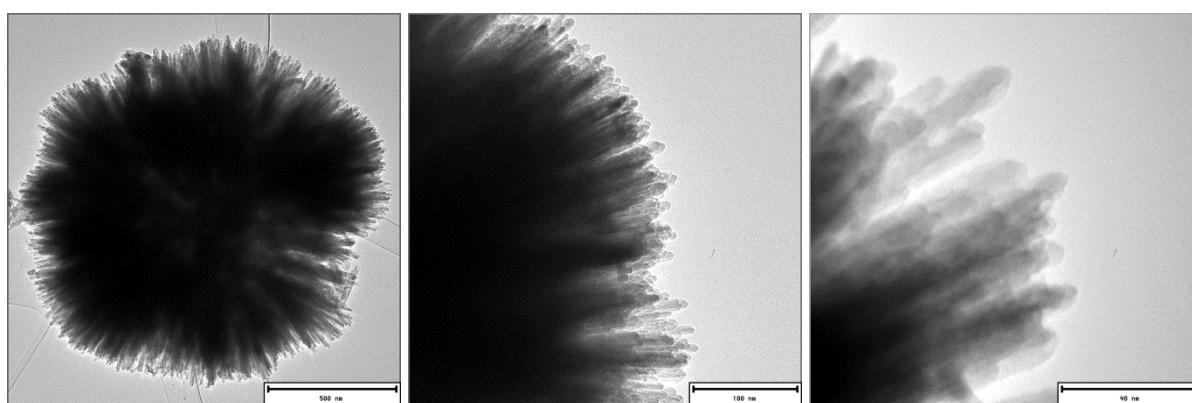
TEM micrographs of Au, Ni and La range of supported catalysts prepared by DPU. The data is incorporated to corroborate the detailed representations about catalysts distribution on the RANR support. The data also support the narrow particle size distribution across all compositions and augment the understanding of the topological effect provided by the RANR structure.



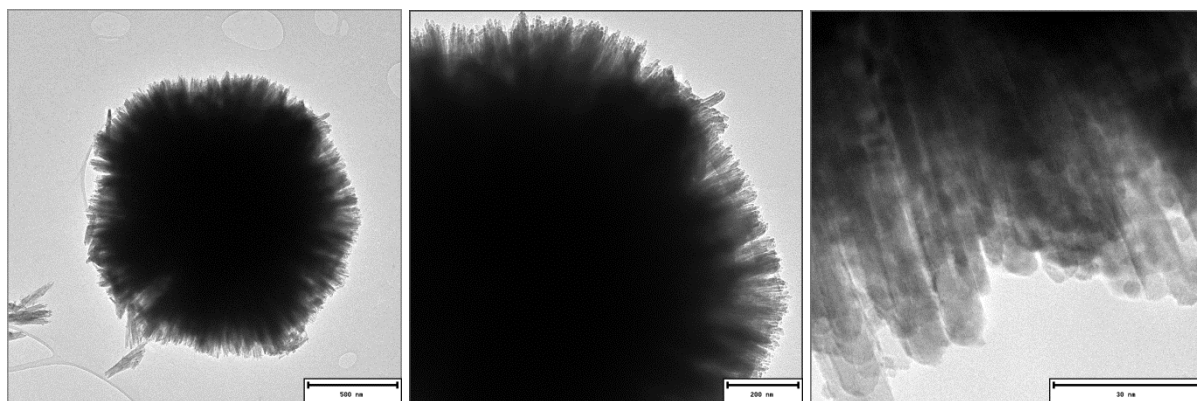
TEM micrographs of 5 wt. % La/RANR catalyst calcined at 500 °C for 1 h.



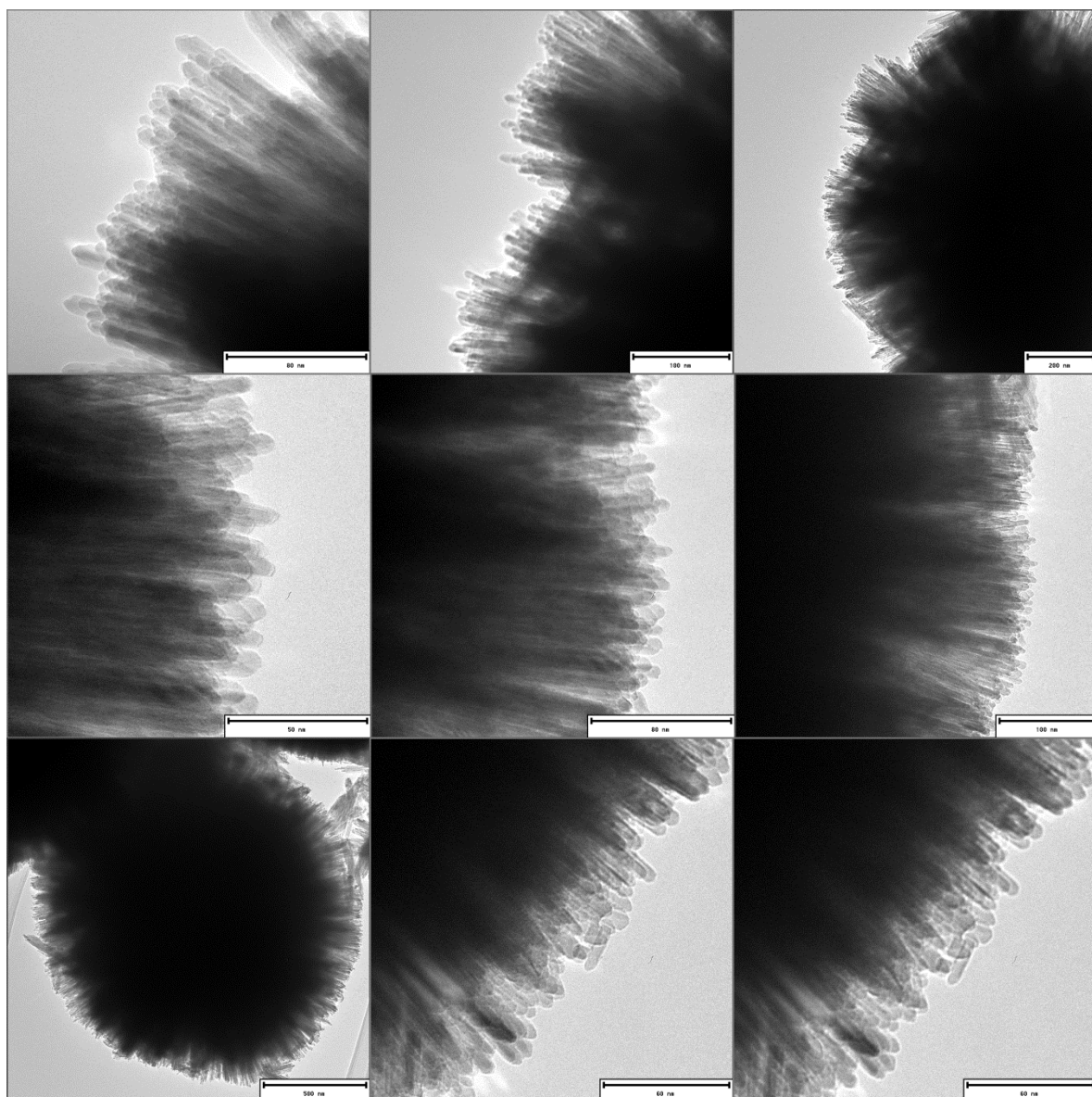
TEM micrographs of 8 wt. % La/RANR catalyst calcined at 500 °C for 1 h.

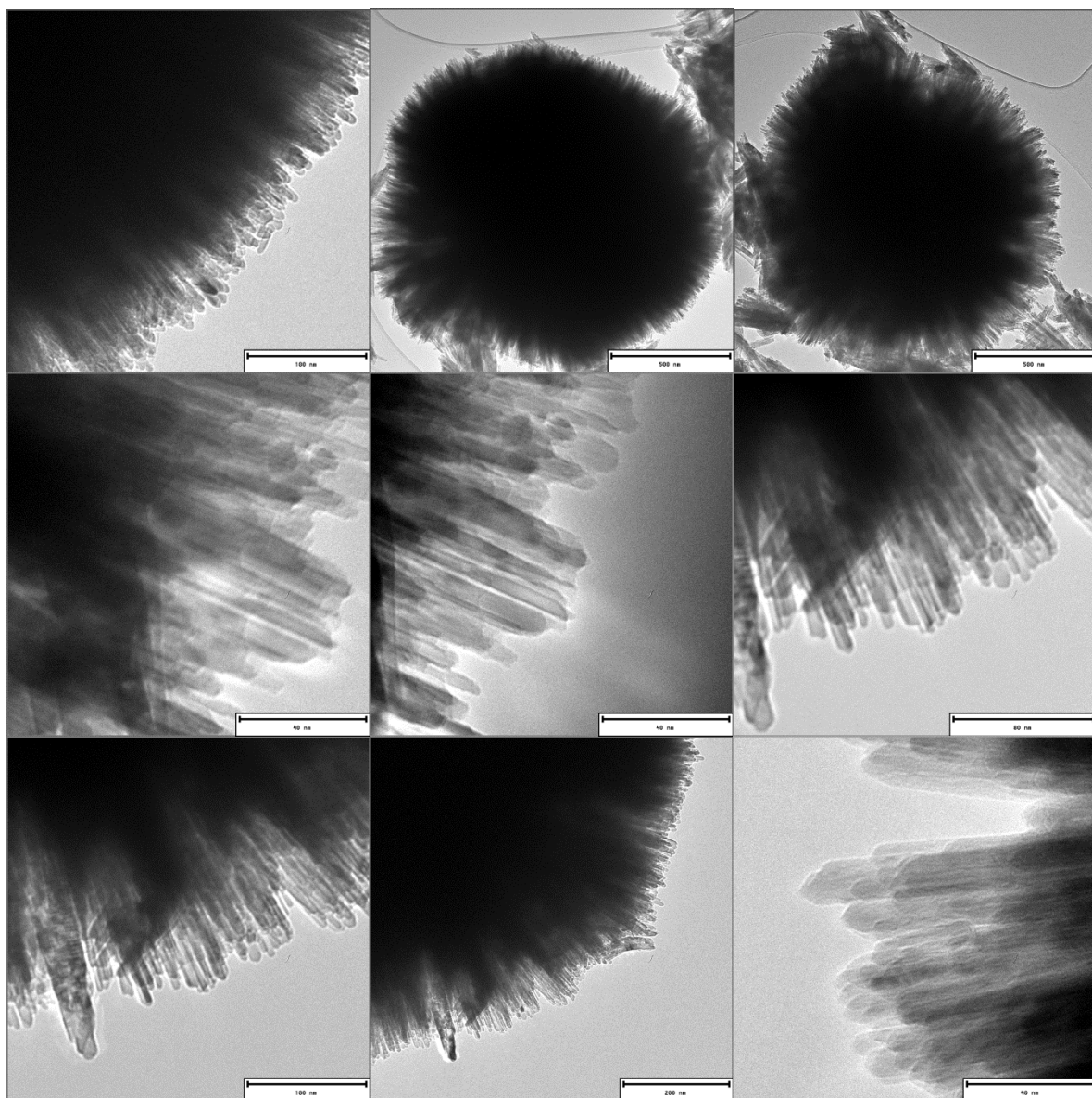


TEM micrographs of 10 wt. % La/RANR catalyst calcined at 500 °C for 1 h.

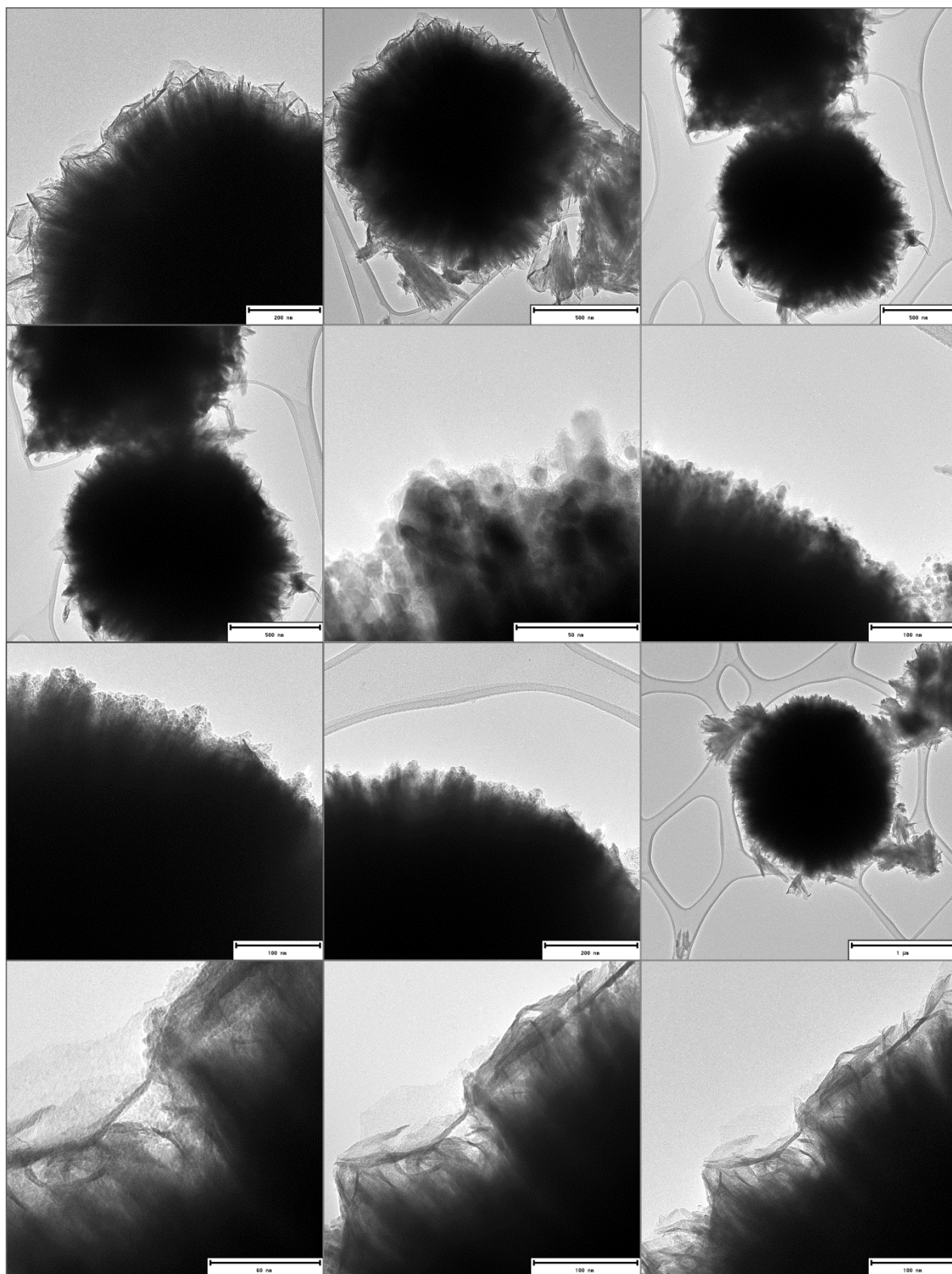


TEM micrographs of 5 wt. % Ni/RANR catalyst calcined at 500 °C for 1 h.

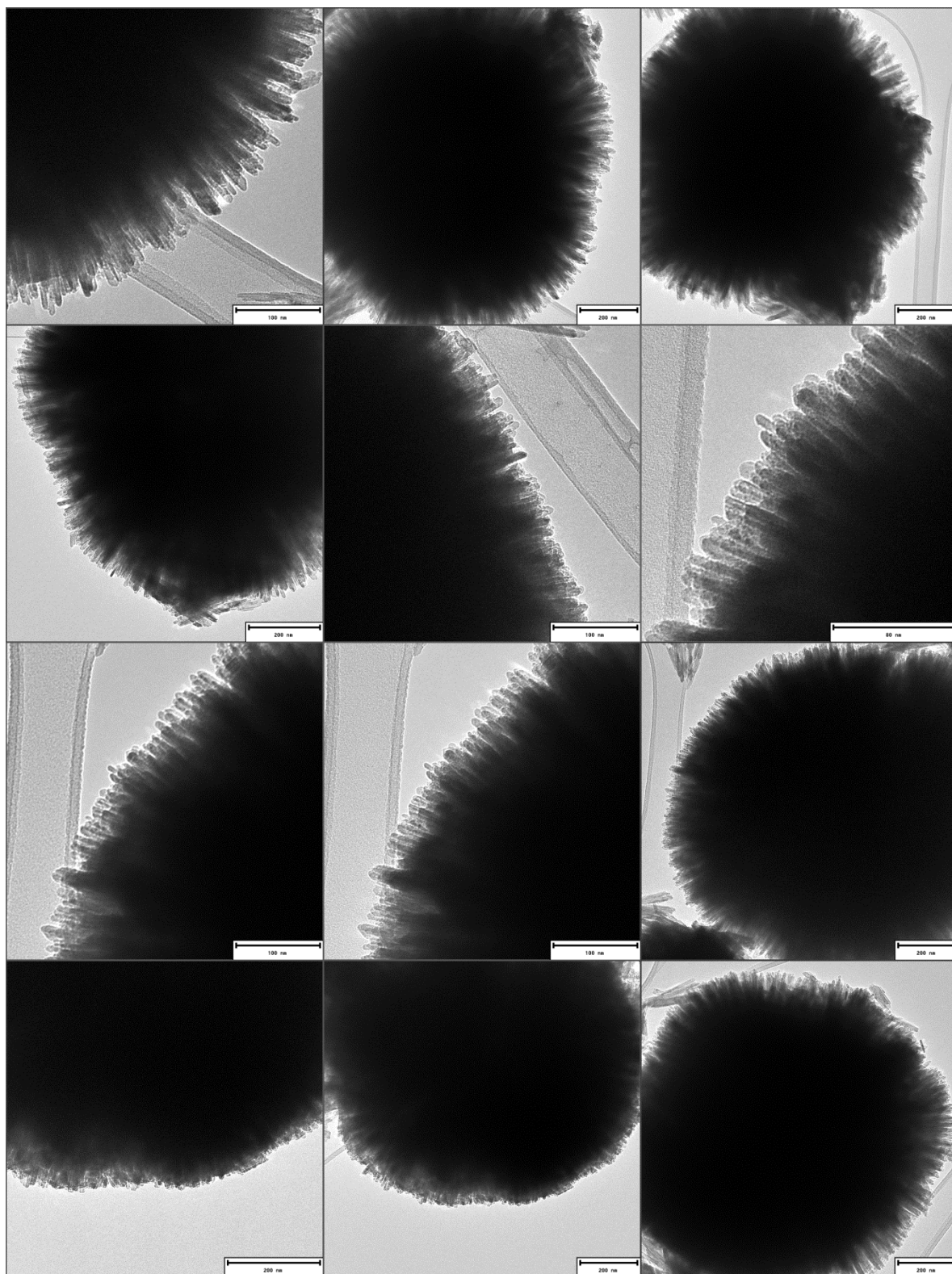




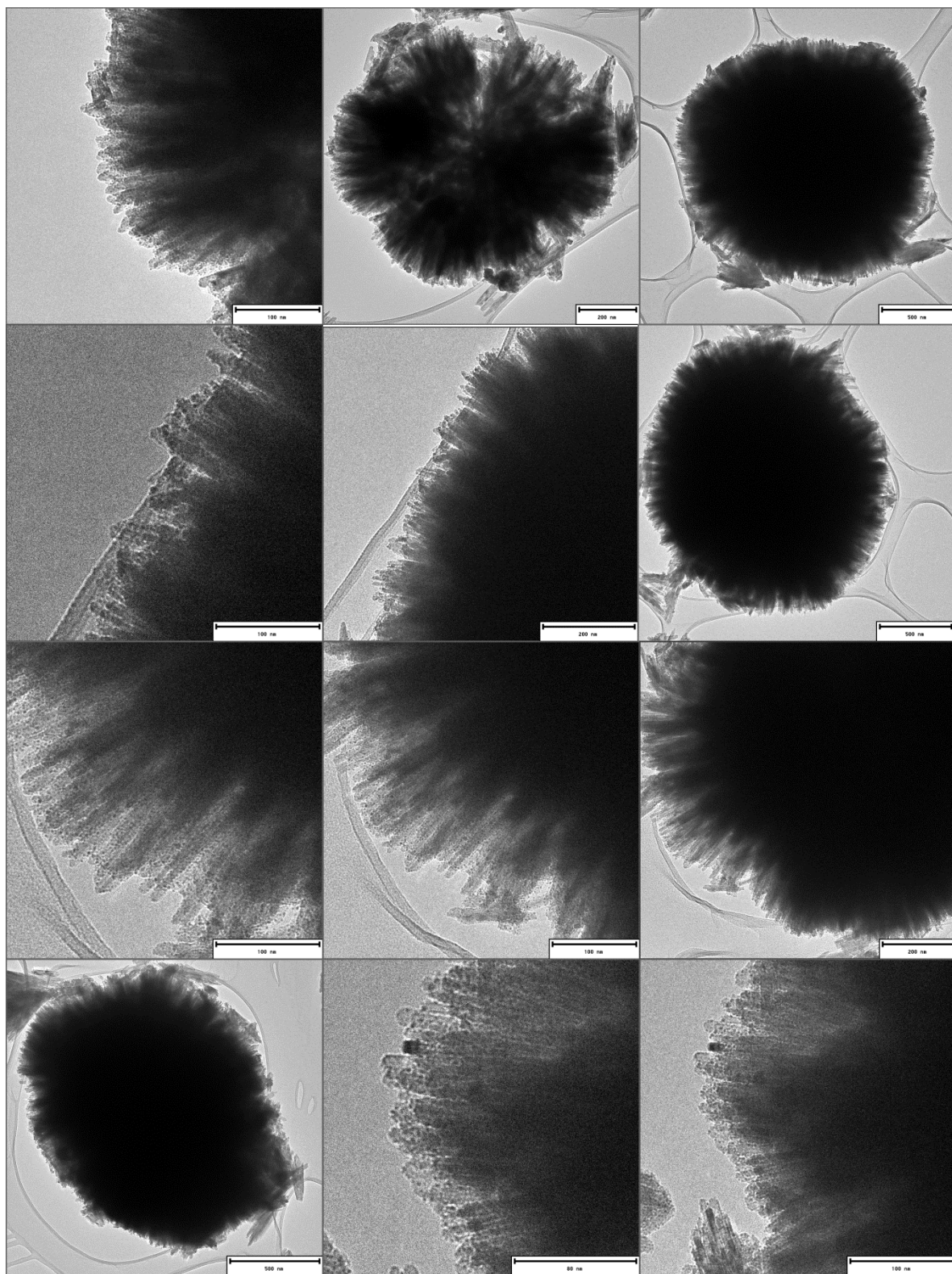
TEM micrographs of 8 wt. % Ni/RANR catalyst calcined at 500 °C for 1 h.

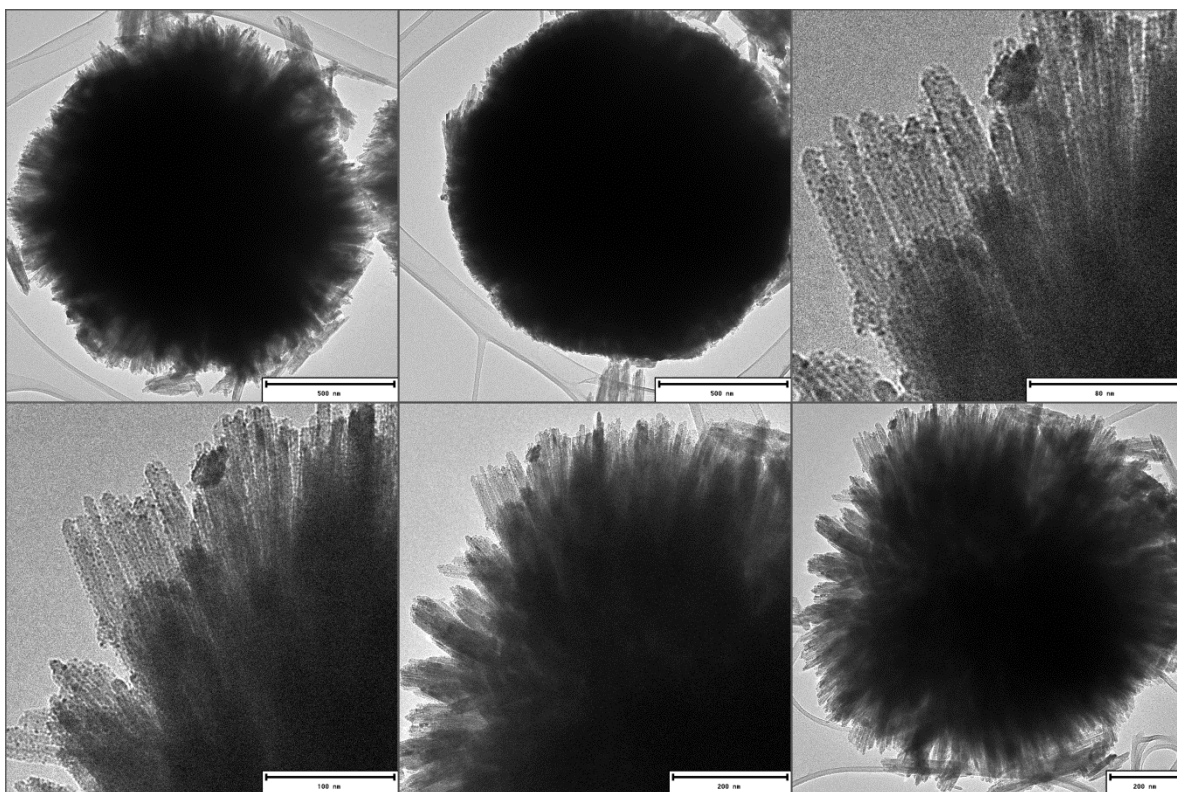


TEM micrographs of 10 wt. % Ni/RANR catalyst calcined at 500 °C for 1 h.



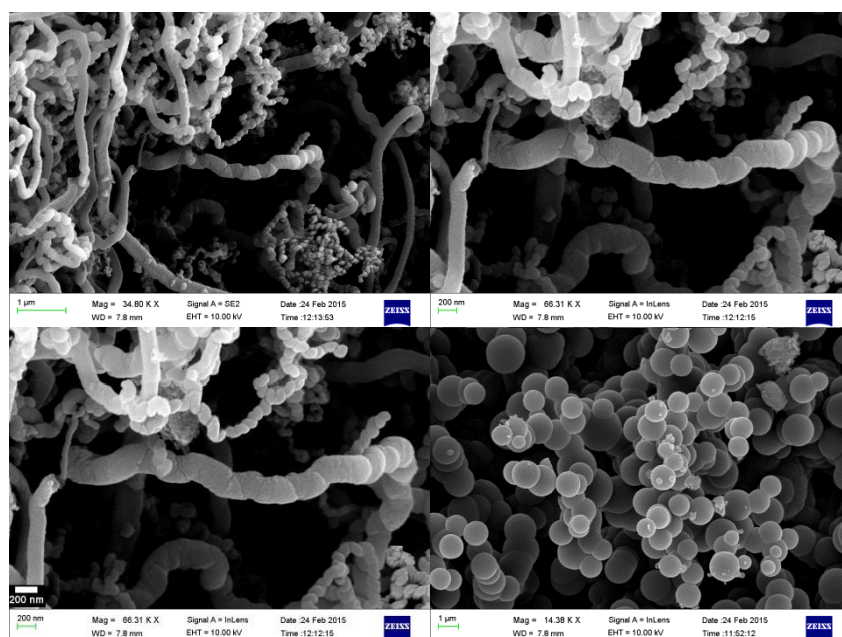
TEM micrographs of 8 wt. % Au/RANR catalyst calcined at 500 °C for 1 h.

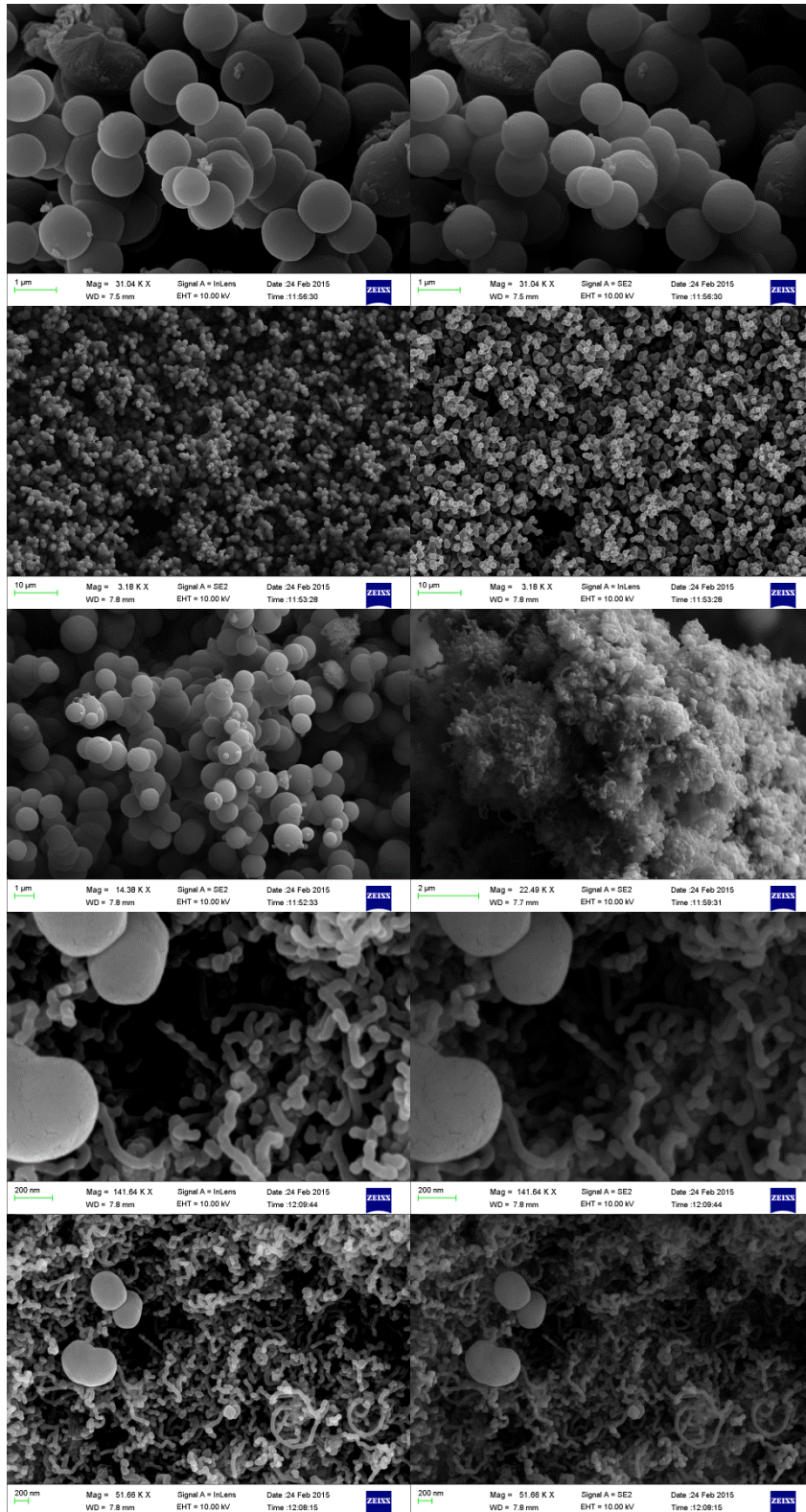


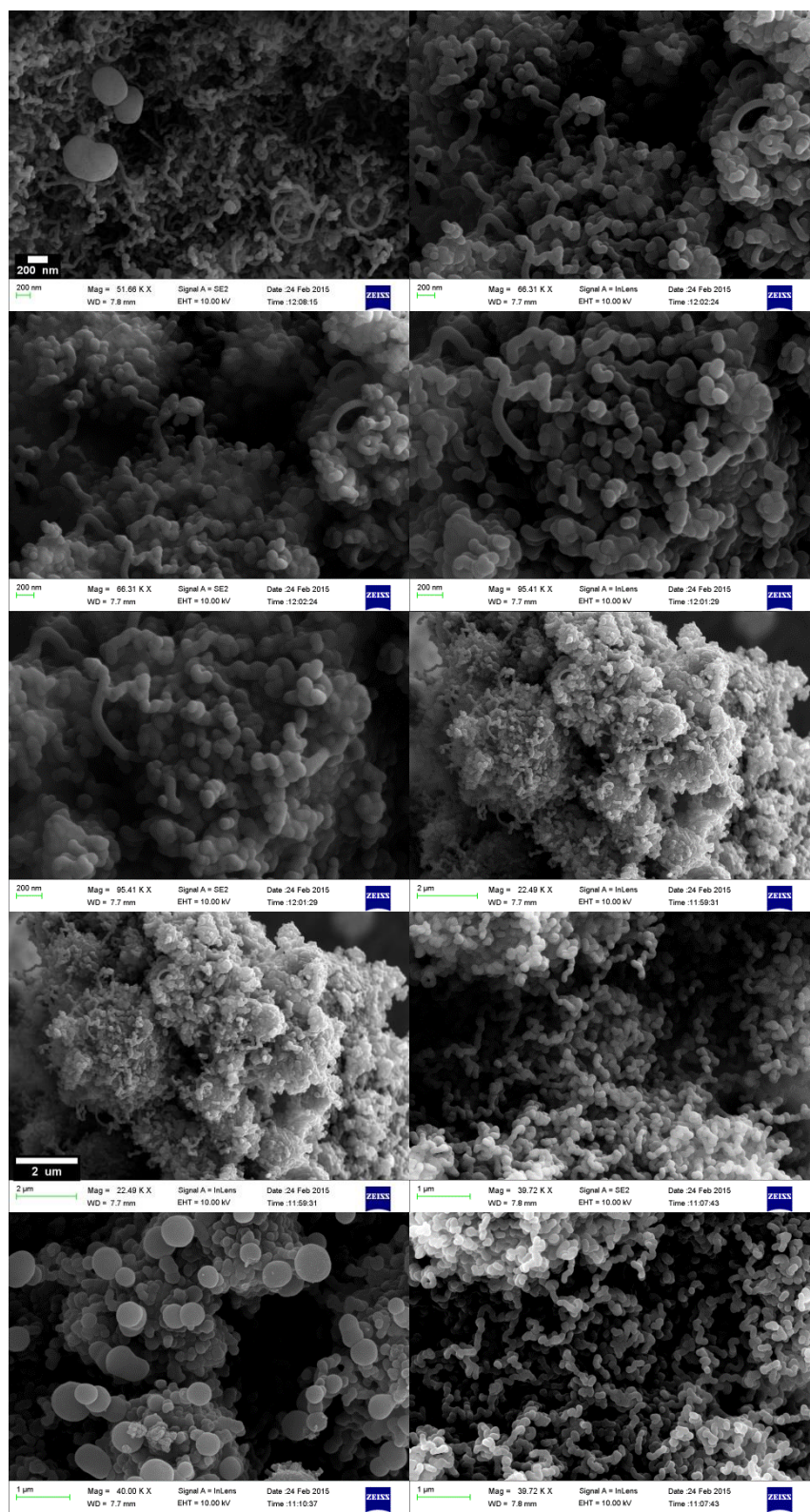


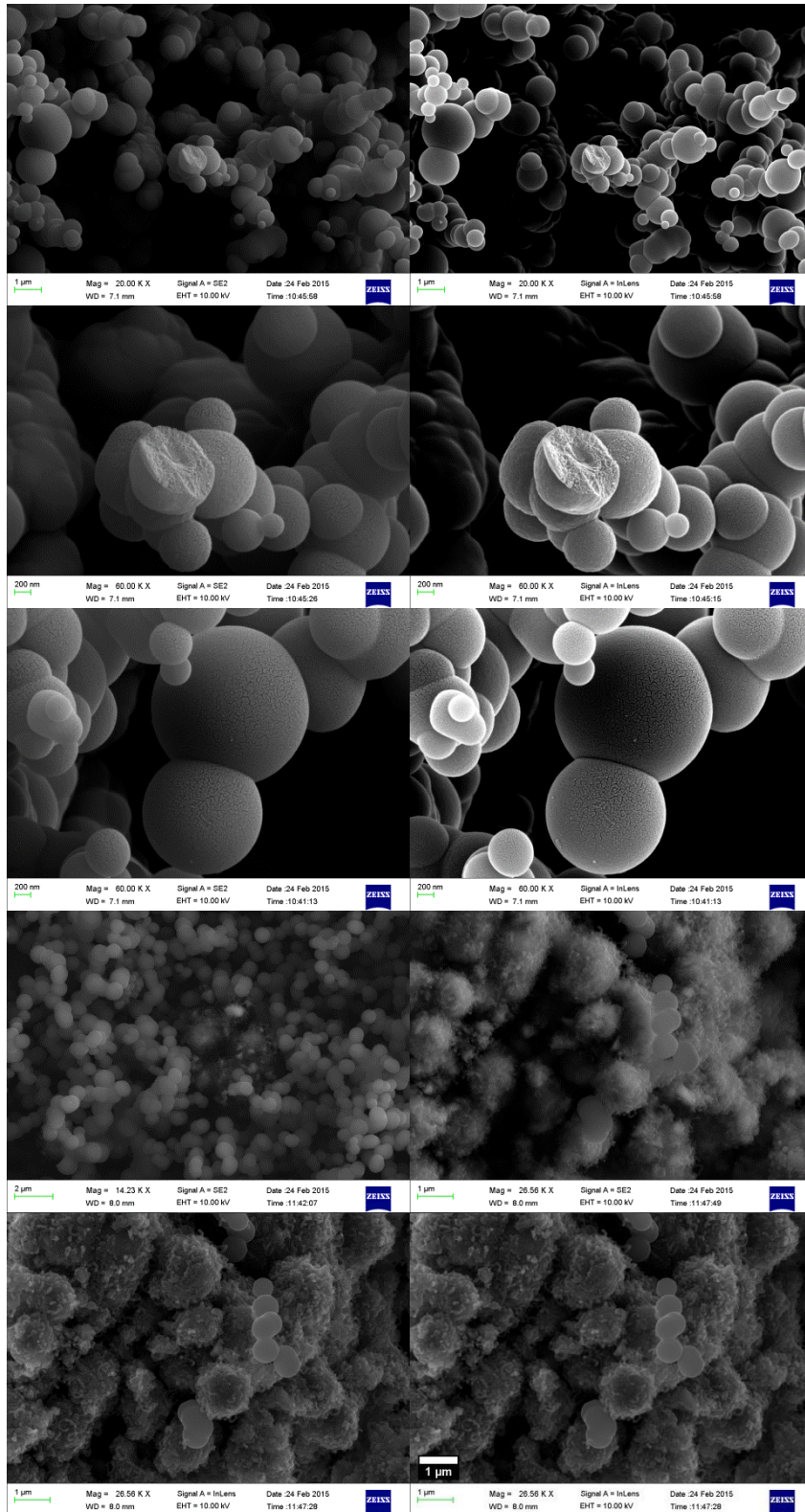
TEM micrographs of 10 wt. % Au/RANR catalyst calcined at 500 °C for 1 h.

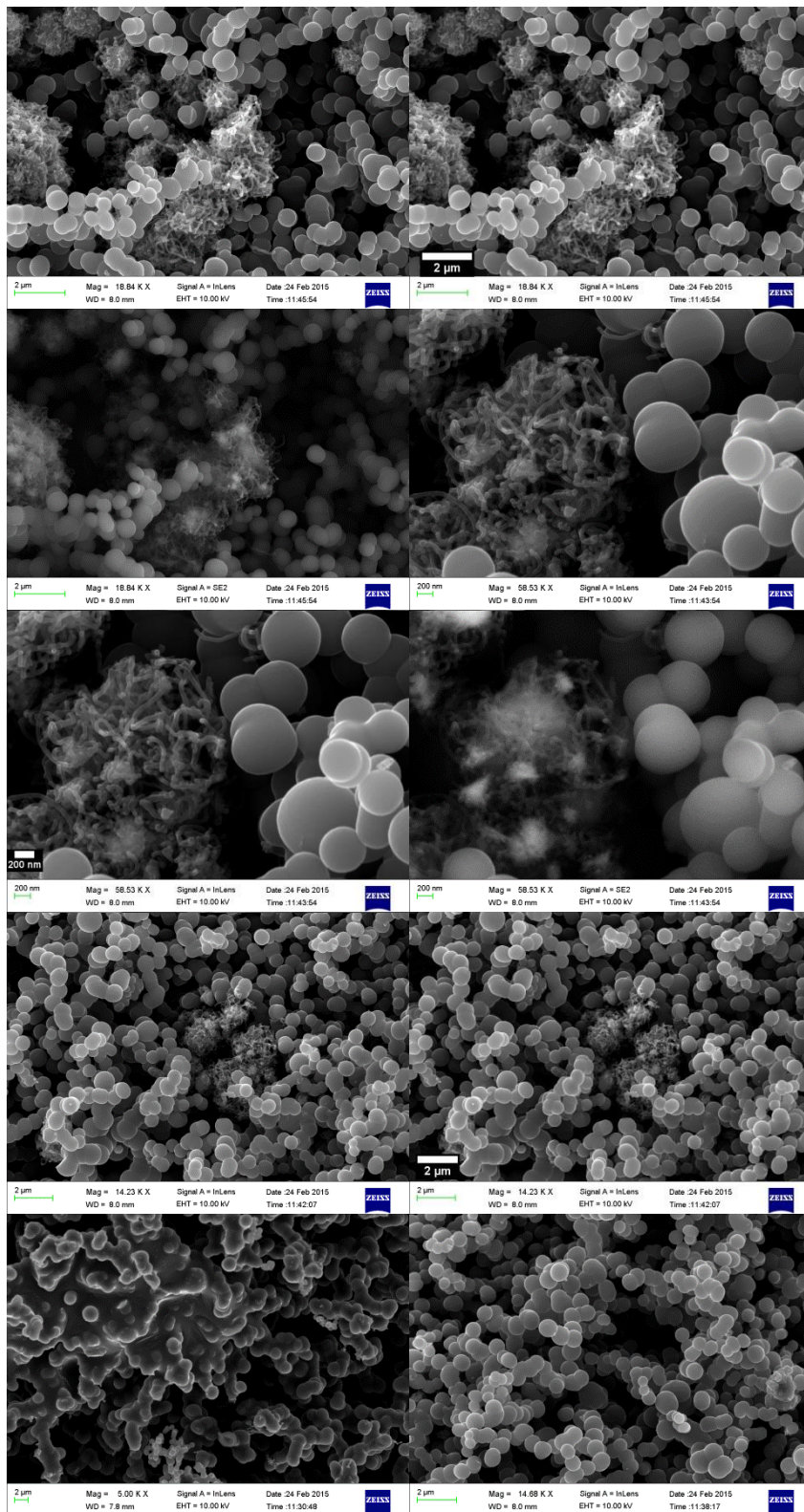
Appendix D

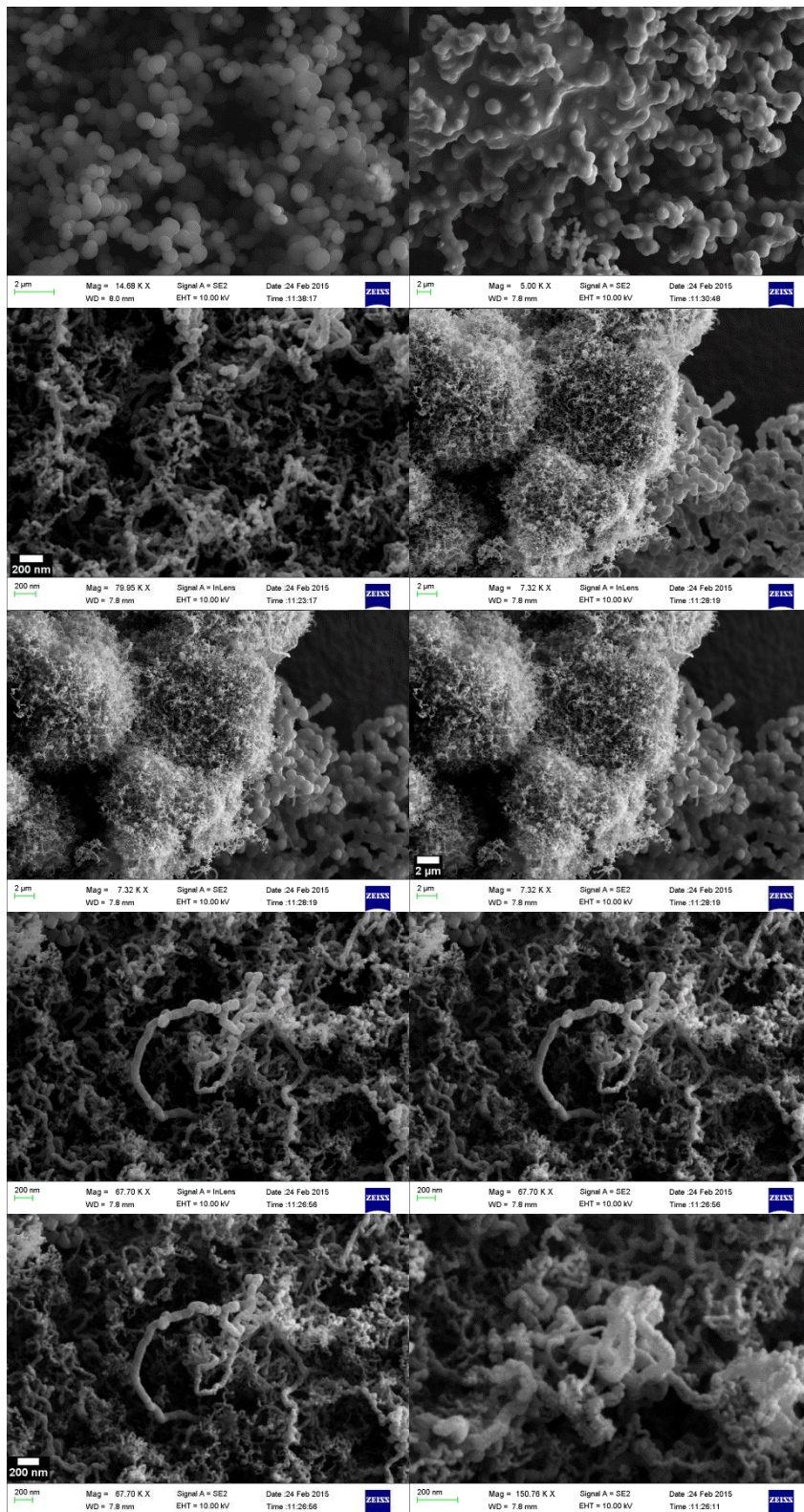


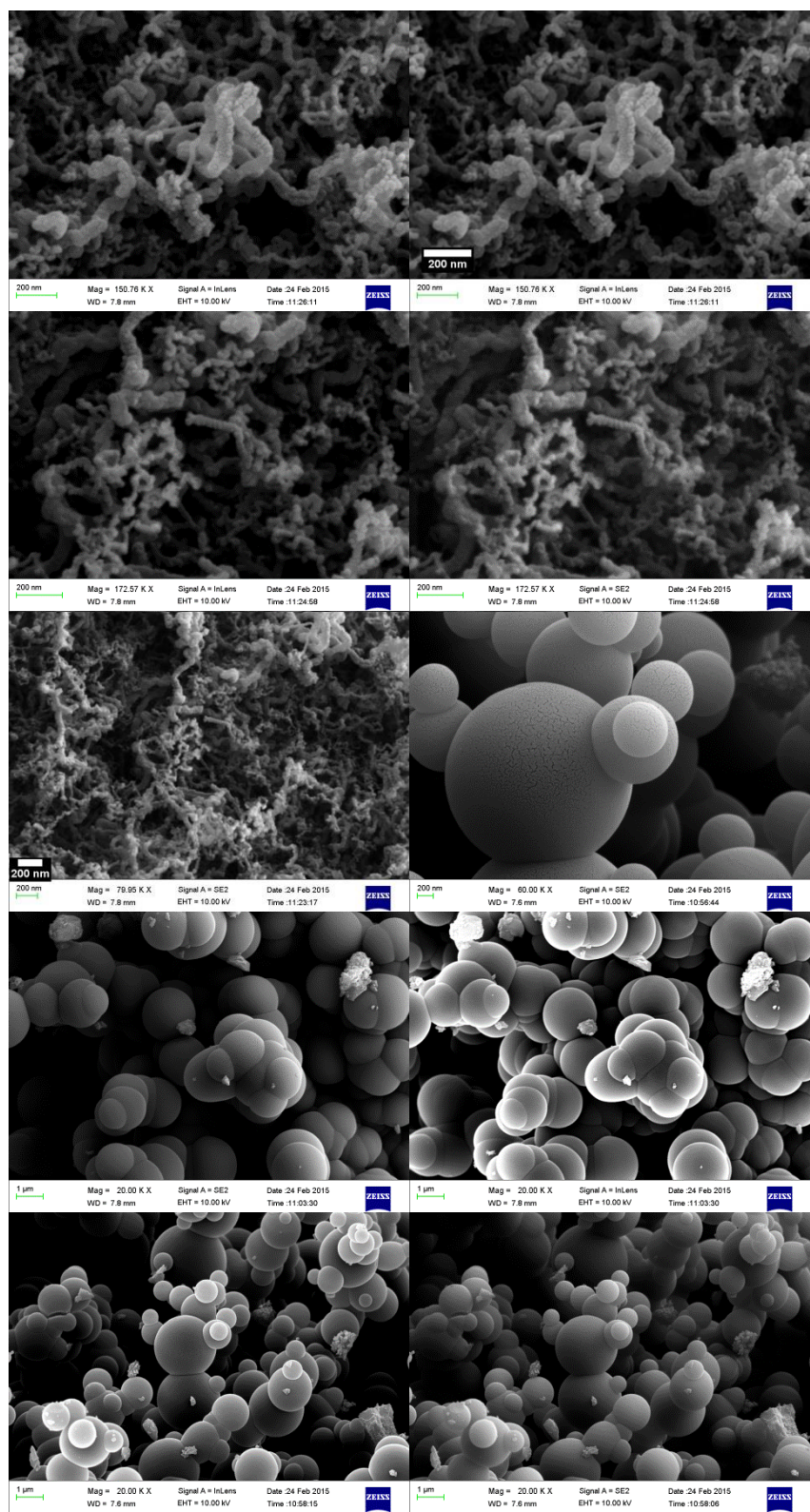


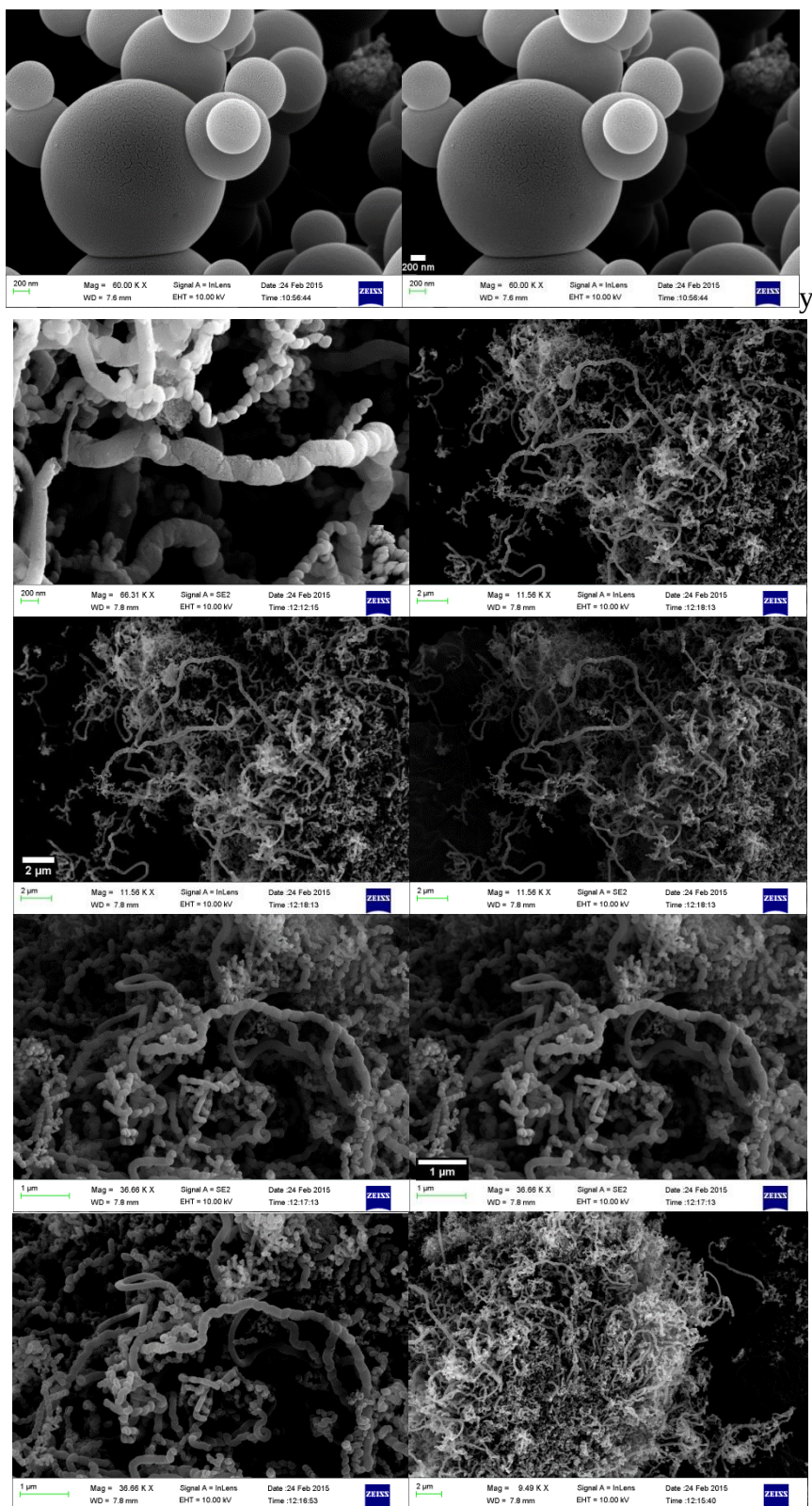


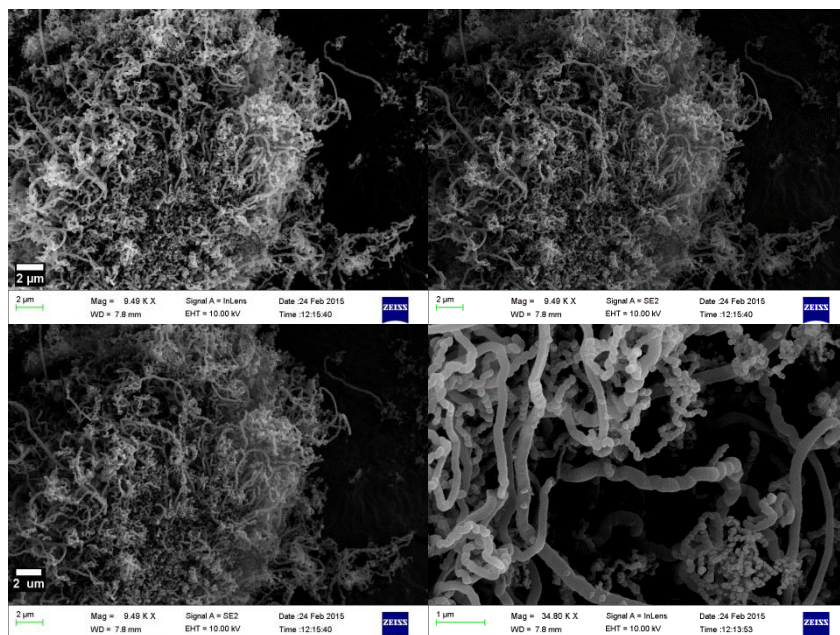












Appendix E

UV- Vis analysis data of low wt. % supported metal photocatalysts for the degradation of MeO.

Std 1	-0.0022				
	-0.0019				
	0.0	-0.0019	0.0003	-14.	-0.0016
Std 2	0.3432				
	0.3434				
	5.0	0.3433	0.0001	0.03	0.3434
Std 3	0.6861				
	0.6856				
	10.0	0.6860	0.0004	0.06	0.6864
Std 4	1.3718				
	1.3719				
	20.0	1.3720	0.0003	0.02	1.3724

Std 5	2.7427
	2.7424
40.0	2.7423 0.0004 0.01 2.7419

Calibration eqn	Abs = 0.06858*Conc -0.00040
Correlation Coefficient	1.00000
Calibration time	2015/09/18 11:16:22 AM

Analysis	
Collection time	2015/09/18 11:16:22 AM

Sample	0.25 wt. % La/RANR	Mean	SD	%RSD	Readings
	ppm				

Sample 1	2.1440
	2.1418
31.3	2.1429 0.0011 0.05 2.1429

Sample 2	0.0845
	0.0741
1.1	0.0743 0.0101 13.5 0.0643

Sample 3	2.1326
	2.1345
31.1	2.1347 0.0023 0.11 2.1371

Sample 4	1.8248
----------	--------

			1.8264		
	26.6	1.8259	0.0009	0.05	1.8264
Sample 5			1.7107		
			1.7123		
	25.0	1.7129	0.0024	0.14	1.7155
Sample 6			1.6968		
			1.6990		
	24.8	1.6993	0.0026	0.15	1.7020
Sample 7			1.5727		
			1.5714		
	22.9	1.5724	0.0009	0.06	1.5732
Sample 8			1.5679		
			1.5662		
	22.9	1.5670	0.0009	0.06	1.5668
Sample 9			0.5875		
			0.5926		
	8.6	0.5927	0.0052	0.87	0.5979
Sample 10			0.5071		
			0.5132		
	7.5	0.5134	0.0064	1.25	0.5199
Sample 11			0.4789		
			0.4805		

7.0 0.4803 0.0012 0.26 0.4813

Sample 12 0.2560

0.2588

3.8 0.2596 0.0041 1.59 0.2641

Sample 13 0.5975

0.5992

8.8 0.6001 0.0031 0.52 0.6036

Sample 14 0.6185

0.6221

9.1 0.6219 0.0032 0.52 0.6249

Read sequence cancelled

Results Flags Legend

U = Uncalibrated O = Overrange

N = Not used in calibration R = Repeat reading

Concentration Analysis Report

Report time 2015/09/23 10:29:01 AM

Method

Batch name C:\Users\Agilent-Guest\Desktop\farai\farai.BCN

Application Concentration 4.20(468)

Operator

Instrument Settings

Instrument	Cary 100
Instrument version no.	12.00
Wavelength (nm)	464.00
Ordinate Mode	Abs
SBW (nm)	1.5
Ave Time (sec)	0.100
Beam mode	Double auto select
Beam interchange	Normal
Replicates	3
Standard/Sample averaging	OFF
Weight and volume corrections	OFF
Fit type	Linear
Min R ²	0.95000
Concentration units	ppm

Comments:

Zero Report

Read	Abs	nm
Zero	(0.0682)	464.00

Calibration

Collection time 2015/09/23 10:29:06 AM

Standard	0.5 wt. % Ni/RANR	Mean	SD	%RSD Readings
----------	-------------------	------	----	---------------

ppm

Std 1	-0.0003
	-0.0004
0.0	-0.0001 0.0004 >100 0.0004

Std 2	0.3366
	0.3368
5.0	0.3367 0.0001 0.04 0.3367

Std 3	0.6517
	0.6525
10.0	0.6524 0.0006 0.10 0.6530

Std 4	1.3538
	1.3547
20.0	1.3543 0.0005 0.03 1.3543

Std 5	2.6138
	2.6190
40.0	2.6166 0.0026 0.10 2.6171

Calibration eqn Abs = 0.06556*Conc +0.00859

Correlation Coefficient 0.99963

Calibration time 2015/09/23 10:35:41 AM

Analysis

Collection time 2015/09/23 10:35:41 AM

Read sequence cancelled

Results Flags Legend

U = Uncalibrated O = Overrange

N = Not used in calibration R = Repeat reading

Concentration Analysis Report

Report time	2015/10/01 08:38:56 AM
Method	C:\Users\Agilent-Guest\Desktop\farai UV - Analyses\Photodegradation of MeO Farai.MCN
Batch name	C:\Users\Agilent-Guest\Desktop\farai UV - Analyses\Plain rutile TiO2 Dandelions1.BCN
Application	Concentration 4.20(468)
Operator	

Instrument Settings

Instrument	Cary 100
Instrument version no.	12.00
Wavelength (nm)	464.00
Ordinate Mode	Abs
SBW (nm)	1.5
Ave Time (sec)	0.100
Beam mode	Double auto select
Beam interchange	Normal
Replicates	3

Standard/Sample averaging OFF

Weight and volume corrections OFF

Fit type Linear

Min R² 0.95000

Concentration units ppm

Comments:

Calibration

Collection time 2015/10/01 08:39:00 AM

Standard	Concentration	F	Mean	SD	%RSD	Readings
	ppm					

Std 1				0.0819		
				0.0818		
	0.0	0.0821	0.0004	0.55	0.0826	

Std 2				0.4145		
				0.4139		
	5.0	0.4144	0.0005	0.11	0.4149	

Std 3				0.7323		
				0.7331		
	10.0	0.7330	0.0007	0.09	0.7337	

Std 4				1.4352		
				1.4345		
	20.0	1.4354	0.0010	0.07	1.4364	

Std 5	1.4379
	1.4386
40.0	1.4387 0.0008 0.06 1.4396

Calibration eqn	Abs = 0.03410*Conc +0.30919
Correlation Coefficient	0.78689

Min R2 test failed

Results Flags Legend

U = Uncalibrated O = Overrange
 N = Not used in calibration R = Repeat reading

Concentration Analysis Report

Report time	2015/09/19 12:46:49 PM
Method	
Batch name	C:\Users\Agilent-Guest\Desktop\farai\La-TiO2 analysis.BCN
Application	Concentration 4.20(468)
Operator	

Instrument Settings

Instrument	Cary 100
Instrument version no.	12.00
Wavelength (nm)	646.00

Ordinate Mode	Abs
SBW (nm)	1.5
Ave Time (sec)	0.100
Beam mode	Double auto select
Beam interchange	Normal
Replicates	3
Standard/Sample averaging	OFF
Weight and volume corrections	OFF
Fit type	Linear
Min R ²	0.95000
Concentration units	g/L

Comments:

Zero Report

Read	Abs	nm
Zero	(0.0639)	646.00

Calibration

Collection time 2015/09/19 12:47:01 PM

Standard	0.5 wt. % Ni/RANR	Mean	SD	%RSD	Readings
g/L					
Std 1		0.0012			
		-0.0004			
	0.0	0.0001	0.0010	>100	-0.0006

		0.0020			
	34.6	0.0017	0.0003	15.7	0.0015
Sample 2			0.0018		
			-0.0778		
	30.1	-0.0513	0.0460	-89.	-0.0780
Sample 3			-0.0026		
			-0.0024		
	27.6	-0.0024	0.0002	-10.	-0.0021
Sample 4			0.0031		
			0.0039		
	22.5	0.0035	0.0004	12.6	0.0035
Sample 5			-0.0005		
			0.0000		
	20.0	-0.0002	0.0003	>100	-0.0001
Sample 6			0.0011		
			0.0002		
	19.6	0.0007	0.0004	60.1	0.0008
Sample 7			0.0025		
			0.0031		
	9.1	0.0036	0.0014	40.0	0.0052
Sample 8			-0.0034		
			-0.0019		

	8.0	-0.0021	0.0012	-55.	-0.0011
Sample 9			0.0168		
			0.0165		
	7.3	0.0168	0.0003	1.89	0.0171
Sample 10			0.0083		
			0.0083		
	6.1	0.0080	0.0006	7.01	0.0073
Sample 11			0.0029		
			0.0031		
	5.8	0.0028	0.0004	13.0	0.0024
Sample 12			0.0026		
			0.0023		
	3.8	0.0031	0.0011	36.4	0.0044
Sample 13			-0.0001		
			0.0001		
	2.9	0.0002	0.0004	>100	0.0006
Sample 14			0.0010		
			0.0018		
	1.8	0.0016	0.0005	33.0	0.0020
Sample 15			0.0044		
			0.0038		
	1.3	0.0038	0.0005	13.8	0.0033
Sample 16			0.0015		
			0.0034		
	0.7	0.0030	0.0014	45.9	0.0042

Read sequence cancelled

Results Flags Legend

U = Uncalibrated O = Overrange

N = Not used in calibration R = Repeat reading