

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

First Examiner's corrections

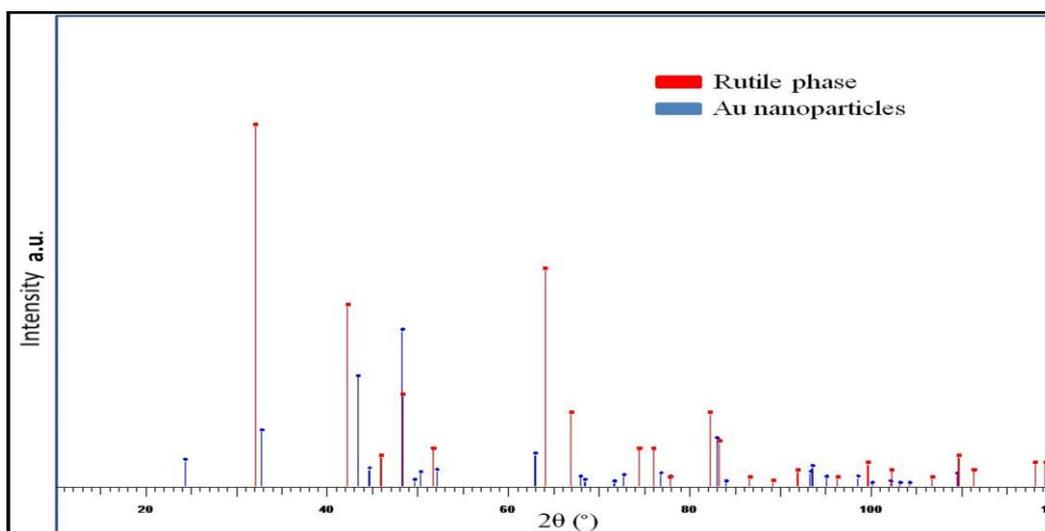
- 1. In the thesis abstract (page 9), regarding the characterization of materials, the scholar has discussed the trend (increase/decrease) of the material property, the reason for the trend should be clarified.**
 - The trend was explained as: *BET surface area analysis showed the Metal/RANR catalyst decreased from 50 to 33 m² 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.*
- 2. Clarify the selection of Au, Ni, La and the mixed metal (La-Ni) for the study.**
 - *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.*
- 3. In page 51, mention the amount of metal precursor added.**
 - *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 x 10⁻³ M H₂AuCl₄), (0.408917g NiNO₃·6H₂O), (0.14268g LaCl₃) and urea (0.42 M). The precursor metal compounds in the solution corresponded to 8 wt. %.*
- 4. Page 55, what is the purpose of having the non-calcined material.**
 - *Both calcined and non-calcined samples were prepared in this way for control purposes and tracking phase transitions during calcination.*
- 5. Page 75, the purpose of addition of urea is to be justified by experimental data.**
 - *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).*
- 6. What is the significance of deposition time?**
 - *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. 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.¹*

- 7. Even at higher magnification, the Ni and La metal nanoparticles are light but contrast sufficiently from the RANR to be distinguished.** Corrected to:-
- *Even at higher magnification, the Ni and La metal nanoparticles are light and do not contrast sufficiently from the RANR to be distinguished.*
- 8. In the XRD patterns, how are the peaks pertaining to the supported metal are assigned? Should be supported by JCPS or references.**
- *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 from metallic gold (ICSD collection code 44362). The peaks at 2θ values 45 and 52.1° increase in intensity with an increase in wt. % metal 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.*
- 9. Page, 94, conclusions. The + comprises means?**
- 10. In page 132, fig. 6.1 in y-axis, the intensity is represented in cps or arbitrary units and the unit of x-axis is no presented.**
- *Unit of the x-axis for the PXRD presented as 2θ .*
- 11. In page 51, what is the amount of urea added?**
- *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).*
- 12. In page 77, represent the miller indices in the correct format.**
- *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.²*
- 13. In page 145, the thermogram reasoning on the loss of weight is not convincing. The discussion on TGA needs to be changed.**
- *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 the higher the 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°C 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 for 8 and 10 wt. % La/RANR showed decomposition taking 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 limits. This material may be attributed to both catalyst material and possibly temperature enhanced highly stable graphitised materials.*

14. Page 156, Fig 7.1 again check the intensity.



15. Where metal has been supported, it is important to give the % composition of the elements obtained by the analytical techniques.

- *corrected*

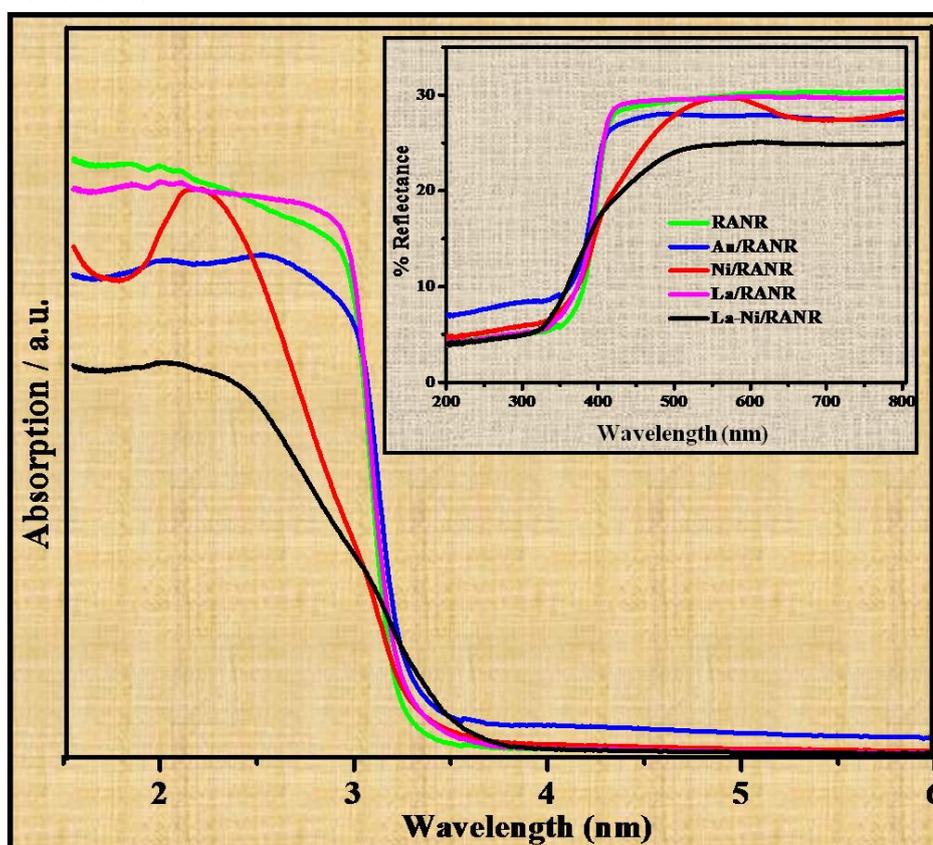
16. Page 188, check the xrd pattern.

- *Corrected*

17. What are the oxidation states of the metal (s) in the entire set of materials? Any XPS study carried out?

- *Metal catalysts were loaded as metal hydroxide on RANR. Upon reduction in H₂ gas, the metals hydroxides were reduced to metallic nanoparticles to give Au/RANR, La/RANR, Ni/RANR and La-Ni/RANR.*

18. Chapter 9. Page 216, check the unit representation of wavelength and wavenumber.



- *Corrected*

19. Page 92 the line “the Pl.... 1000 nm”, but the fig is not present in the said range in fig. 9.2, intensity is represented as a.u.

- *Fig. 9.2 showed the major peak occurring around 420 nm within a 380 – 470 nm spectral range.*

20. Regarding the photocatalytic activity, is it degradation/demineralisation or decolourization?

- *The reaction is photodegradation of organic water contaminants. MeO was used as a controlled contaminant.*

21. If the process is degradation study, COD analysis is very important.

- *The chemical oxygen demand (COD) is an indicative measure of the amount of oxygen that can be consumed by reactions in a measured solution. It is commonly*

expressed in mass of oxygen consumed over volume of solution which in SI units is milligrams per litre (mg/L). A COD test can be used to easily quantify the amount of organics in water. However this research needed not measure the amount of organics since the concentration of MeO was deliberately controlled.

22. The plain RANR is capable of degrading the MeO completely, but the synthesized material failed. Then how do you justify that the prepared material is superior to the virgin material?

- Plain RANR exhibited better photocatalytic activity than all the supported catalysts, a phenomenon reported in many similar previous works.

23. What about the recyclability of the catalyst?

- Recyclability of the catalyst was not part of the study of this research.

Second Examiner's corrections

1. Remove full-stop from title

- Full-stop removed from the title

2. the solution's pH value result in RANR at various stages of formation

- "the solution's pH value resulted in RANR at various stages of formation"

3. Explain why the synthesis of CNFs from the decomposition of acetylene and hydrogen (H_2/C_2H_2) was targeted

- 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.

4. In this work, RANR were prepared in such that a way that the rutile nanorods that formed had an average diameter of 5–8 nm

- "In this work, RANR were prepared in such a way that the rutile nanorods that formed had an average diameter of 5–8 nm"

5. Aim and Objectives

- Corrected to "Aim and Objectives"

6. Objectives: Add full-stops after each objective.

- Corrected.

7. Reference 5 and 6 are the same

- References fixed.

8. Check reference 3 and fix.

- 73 corrected to 3.

9. Titles are not presented in a consistent way in the reference. This applies to other chapters. The candidate must fix this.

- Titles in references corrected.

10. Remove full-stop on heading.

- Full-stops removed on headings.

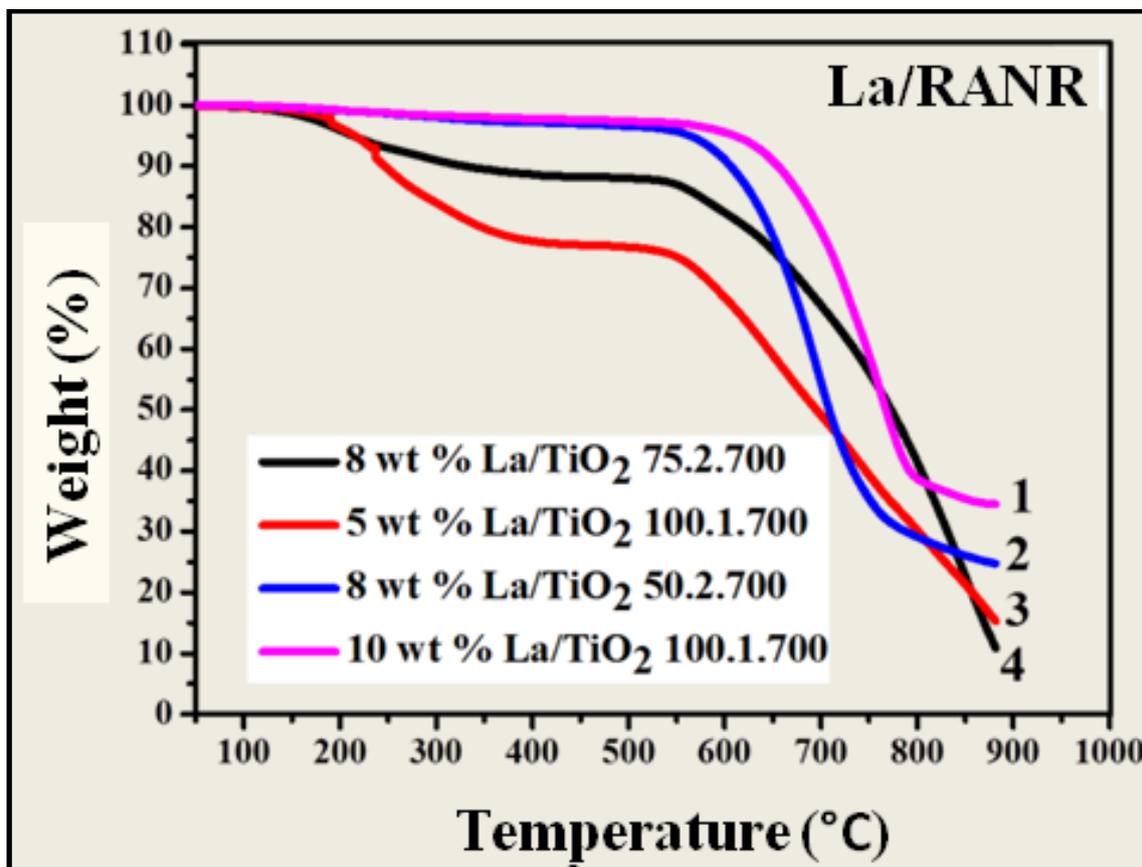
11. Fig 5.4 should be bold.

- This is evidenced by the high diameter sized particles observed after the synthesis of CNFs (Fig. 5.4).

12. Gas Flow rates variation

- Corrected to "Gas Flow rates"

13. Figure 5.12: What is the meaning of the brackets?



14. Fix references on lines 10, 11 and 13.

- References fixed.

15. Fix 100 mL min⁻¹

- Spacing fixed

16. Remove full-stop on Chapter 7 title.

- Full-stop removed.

17. Literature Review

- Corrected to "Literature review"

18. Fix the word "ti tania"

- Spacing removed "titania"

19. Rephrase "At all times, the furnace's temperature was ramped up....."

- Statement rephrased to read "At all times, the temperature of the furnace was ramped up....."

20. Table 7.3: there is no explanation why I_D/I_G ratio decreases.

- 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.

21. Gas Flow rates and Time variation

- Corrected to ***“Gas Flow rate and Time variation”***

22. Move 10.2 to top of page.

- Page alignment corrected.

Third Examiner’s corrections

1. The font size in many figures is too small.

- Font size in most figures increased.

2. Justification needs to be inclusive of the choice of catalysts to make the carbons.

- Research justification extended to include: *‘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.’*

3. Much of the information on the photocatalytic behaviour of the M/TiO₂ seems out of place.

- The chapter was extended with section 2.4 titled *“Photocatalysis studies”*.
-

4. It is not clear what information section 4.1 is trying to convey. Is it needed?

- *RANR have been prepared for use in photocatalytic reactions.³ 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.* -: Served as the chapter abstract that pointed out why the metals selected in this research.

5. Section 4.2 is missing information.

- *The thesis chapters were compiled as papers for publication for each respective work. The detailed review was done in the subsequent chapters in which the materials were used as catalysts for the synthesis of shaped carbon nanomaterials.*

6. Last line p81, where is the quantitative data?

- Quantitative data was given in the next 5 lines on p82 that followed. *“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.”

7. For TPR curves, need to use area to make statements i.e. quantify the effect

8. Need to comment on the TPR peak found on rutile

- *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 TiO₂ 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.*

9. You cannot introduce new ideas into a conclusion.

- *Ideas explicitly discussed in the text.*

10. What does “equally spatial distribution” mean?

- *Rephrased to “The deposition of 10 wt. % La showed uniform spatial distribution of La nanoparticles as shown in Fig. 7 (c)”.*

11. The synthesis of La/RANR catalysts on p99 ref. 1 does not relate to carbon synthesis but doping of TiO₂ by C and La.

- *The reference gives a background of previous studies and uses of La. The paragraph that followed state that “based on extensive literature search, it appeared that supported La had never been used unaided as a catalyst in the synthesis of SCNMs”. So this brings out the novelty in the study of the material as a catalyst for CNMs synthesis.*

12. Given that La has not been used before, no reason was given for this study.

- *The reason for studying La was clearly highlighted in Chapter 4 in the statement “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.”*
- *The last statement of the Literature review also points out the primary reason for the study of La as an independent catalyst:- “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”.*

13. A major problem relates to the interpretation of the sintering effect.

- *This is because the La particles sinter during the reaction to form larger sized particles 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 high diameter sized particles observed after the synthesis of CNFs (Fig. 5.4).*

14. While the large size of the CNFs suggests large La particles, these need to be shown. Fig 5.3 and Fig 5.5 do not show La particles.

- *Figures 5.3 (b) and 5.5 (d) shows the sizes of the La particles after having supported tip growth of CNFs. The particle sizes and their corresponding fibre thickness is 51 and 348 nm respectively.*

15. Not sure what Fig 5.3 shows? This need explanation.

- *Page 107, “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)).”*

16. Consequently even though tip growth makes sense – the Figs reported do not show it.

- *The statement explained that “in this work we observed that individual La of the La/RANR catalyst particles does not independently affect the properties of the CNFs synthesised. This is because the La particles sinter 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 high diameter sized particles observed after the synthesis of CNFs (Fig. 5.4).”*

17. P118, I am not sure what is being said here. Are you suggesting the CNFs are packing?

- *The statement was rephrased to say “The packing of the carbon readily became disordered along the c-axis because the C-atoms within the fibrous matrix bonded strongly through sp^2 hybridisation and arranged in a 2D honeycomb network.”*

18. Ni is a well known catalyst for making CNFs with and without a support. Yet no sense of this is given in the introduction.

- *However, linear CNFs have limitations in their resin dominated properties such as interlaminar shear strength or longitudinal fibre compression.⁴ 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.⁵ 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.*

19. P131, not sure what discussion of e/h has to do with synthesis here? Elaborate if important; or delete.

- *The misplaced paragraph was deleted under results and discussion section and presented under literature review.*

20. How does the data compare with what has been done before?

- Ni has never been loaded on RANR and used to synthesise CNFs. It will be unimportant to compare the data with what has been done before since different supports influence and affect a catalyst in many various ways.

21. Need to give a sense of what has been done with Au as a catalyst to make CNFs.

- Chapter 7, section 7.2 was extended to include what has been done with Au as a catalyst to make CNMs -: 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.⁶ 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.⁷ 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.⁸

22. Fig 7.1. Need to see data?

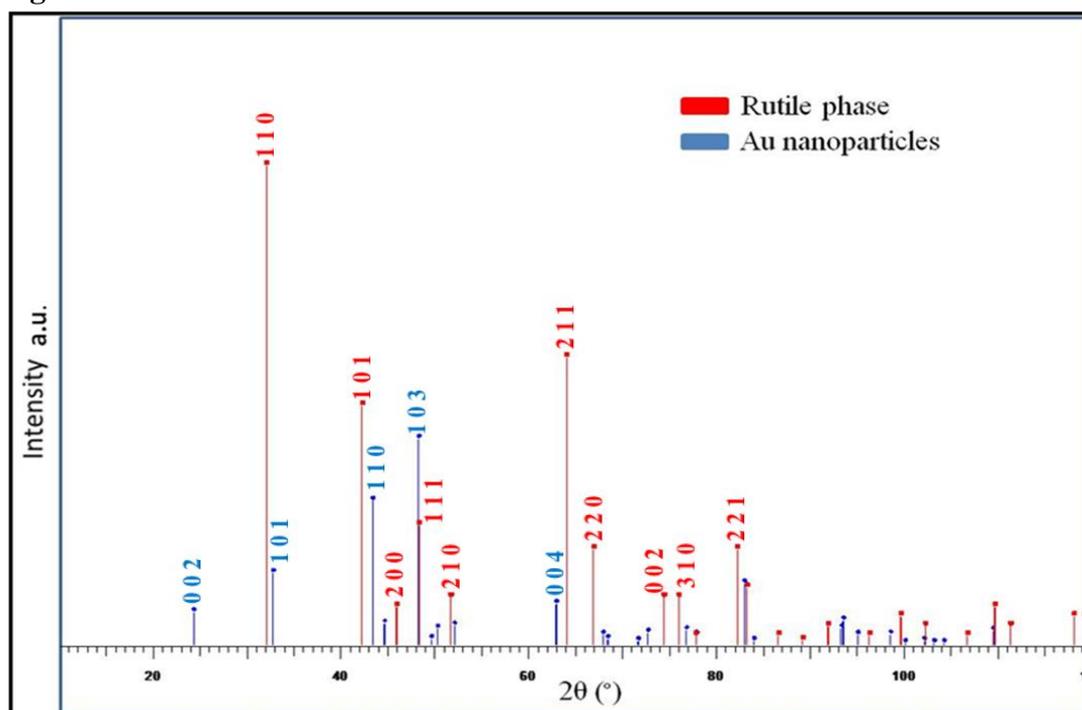


Figure 7.1: A representative PXRD diffractogram of a 5 wt. % Au/RANR catalyst.

23. The effect of a low temperature sintering, but not at high temperature, does not seem correct?

- The interpretation was rectified as follows -: *“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.”*

24. Contradiction in terms of CNFs size/sintering.

- The contradictory statements were rectified to say -: *“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).”*

25. Chapter 8 literature survey is poor and a key reference (perhaps others?) is missing (J Phys Chem. B, 110 (2006) 15284). Literature survey needs to be rewritten.

- Literature review rewritten/extended to include literature review as follows -: *“Zhang et al. studied the catalytic performance of Ni-based catalysts using the support of γ -Al₂O₃·SiO₂ and investigated the effect of the second metal of La, Y, Co, Cu and Zr on catalytic performance of Ni/Al₂O₃·SiO₂ 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/Al₂O₃ and Ni-La/Al₂O₃ 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.”

26. It is not clear as to what has been made: a La/Ni alloy; a separate La + Ni catalyst, a core shell structure. The issue needs to be addressed.

- *Several statements in the text refer to the material as co-loaded La-Ni/RANR catalysts in the introduction, Experimental sections and results sections.*

27. What does a phase diagram add to the decision?

- *The DPU method used was carried out at very low temperatures (80 °C) such that there is completely no possibility of metal fusion taking place to facilitate phase transitions. PXRD analyses after calcinations and reduction also showed that there was no phase transition on the prepared calcinations.*

28. XRD positions can give information about alloys.

- *The peak positions on the PXRD patterns could only be matched to rutile and the respective metals loaded. This was also attributed to the low temperature of catalyst preparation that did not support alloying of metals in the catalyst-support materials.*
-

29. Fig 8.4. Need to compare with pure metals (p93) and discuss.

- *Comparison made as follows -: “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). However, 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, and not comparable to that of pure La/RANR at 600 °C (Fig 4.10c). 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.”*

30. What has not been done – to compare the mix with the single metals? Must be done.

- *Comparisons were made in the text on Section 8.4.3. “Detailed analysis suggests that the coiled fibres disentangled upon sonication in an organic solvent during preparation for TEM analysis. The CNFs are characterised by metal catalysts particles at the tips of the fibres suggesting a bottom-up growth mechanism of fibre development. This also correlated to the growth mechanisms observed in the synthesis of CNFs over La/RANR and Ni/RANR catalysts in Chapters 5 and 6 respectively.”*

31. P212 Doping is used to modify the catalyst behaviour of the TiO₂, a minor issue is the agglomeration. Modify phrase.

- The statement rephrased to say -: *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.*

32. 9.3.1. Move to experimental.

- *Photocatalytic degradation of Methyl Orange (MeO) Section moved to experimental.*

33. Conclusions should be made more quantitative.

- Quantitative data included in the conclusions.

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