NASA

Contents

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1 Introduction

1.1 My Background

I grew up in Trinidad and attended Newtown Girls' R.C School and then St. Joseph's Convent Port of Spain. For the final two years before university, I studied at the International School of Port of Spain. At the University of Leicester, I completed a four year degree program in Natural Sciences. In my final year there, I was introduced to the field of nanomaterial synthesis, and conducted a research project on iron oxide nanoparticle synthesis. After receiving my MSci, I moved to the University of Oxford to pursue a DPhil (PhD) in Material Science. I'm currently entering my 4th year at Oxford, working on carbon and boron nitride nanotube synthesis. I hope that one day these materials will be used in space applications, ranging from multifunctional lightweight materials in astronaut suits to structural and protective materials in spacecraft.

When I'm not doing research, I spend some time volunteering at the Science Innovation Union (SIU) as the editor in chief of our online blog, which is aimed at young academics interested in entrepreneurship and industry.

1.2 Internship Introduction

From the 4th June-9th August 2019, I interned at the NASA Ames Research Center, Mountain View, California. This was my first internship, my first visit to the west coast of USA, my first experience of Silicon Valley and my first time being at NASA! And what a trip it was.

In this report, I summarize my experience with the hope that all those who have supported me can share in my happiness at the outcome of the trip and that I can inspire others to also apply.

Figure 1: Summer Interns Photoshoot. Play a game of can you spot the Trinidadian interns? Saanjali, Gabrielle and I are present. Keanu and Tevin are missing in action. Courtesy NASA AMES

1.2.1 Acknowledgements

Thank you to NIHERST for coordinating this opportunity for citizens of Trinidad and Tobago to participate in the NASA International Internship (I^2) Program. Thank you to everyone in T&T who made this possible, and particularly to Ms Darielle Rampersad for all her prompt correspondence and administration. I would also like to thank the CIEE for supporting and accelerating my exchange visa application.

To my supervisor at NASA, Dr Beomseok Kim, thank you for your friendliness and encouragement. I really felt invigorated by your attentive supervision and your belief in my research abilities. Also thank you to Dr Meyya Meyyappan and Dr Jin-Woo Han for accepting me into your research group and for eagerly responding to my emails or office door knocks. To Ms Porsche Parker, I really appreciated your help with all international intern activities and for making us feel welcomed at NASA.

To my research group mates Gabby and Becca, you both made the experience all the more fun. And to the new friends I made at NASA, I hope to see you again.

Thank you to my best friend and partner Aleksandr for motivating me to apply. To my parents, I cannot express how grateful I am for your support in making this internship a reality.

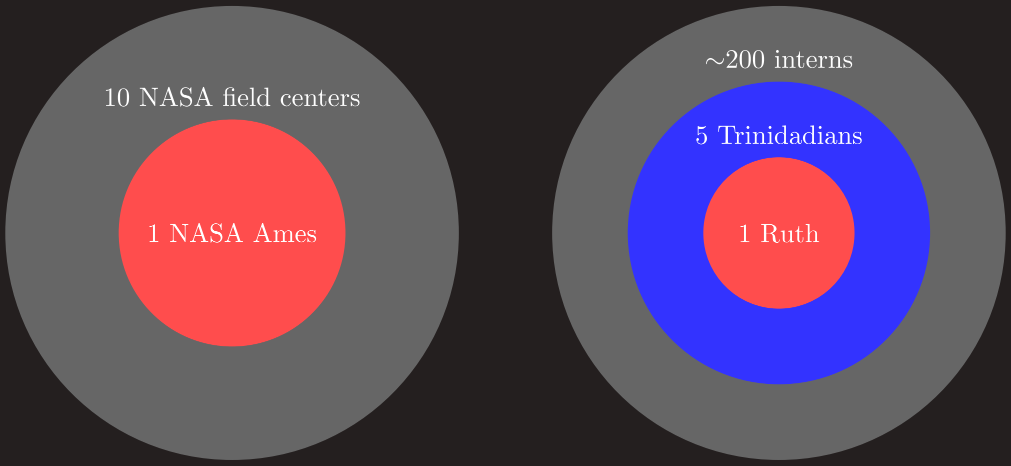


Figure 2: Internship in Numbers

2 Project Summary

2.1 Research Application

Astronauts, Cosmonauts,Taikonauts... all space travellers to the International Space Station breathe the same air in the ISS cabin. Being away from the earth and its natural and abundant atmosphere, the air of the cabin is entirely isolated. This isolation and the dangerous vacuum of outer space already pose hazards to life in space, so it is especially essential to constantly preserve the artificial air environment. Are there sufficient levels of life-supporting gases such as oxygen and water vapour? And are life threatening gases kept below their hazardous thresholds? These are questions that can only be answered if we can make round-the-clock accurate detection of gases in the crew cabin. Doing this requires the implementation of sensors.

Two gases of interest in the ISS cabin are carbon dioxide (CO_2) and ammonia (NH_3). CO_2 is an exhaled product of our metabolism and can accumulate within the cabin if not adsorbed by CO_2 scrubbers. Beyond causing headaches and breathing difficulty, exposure to higher CO_2 concentrations (>5%) in the enclosed cabin can lead to unconsciousness and even death. Whilst CO_2 can accumulate from sources within the cabin, NH_3 can potentially leak into the cabin from the external solar panel cooling system. Exposure can also be fatal to crew, with corrosive effects on the eyes and respiratory system. Furthermore, higher concentrations (e.g 15-28%) can be flammable in air.

There is a need to develop sensors for detecting CO_2 and NH_3 so that emergency situations can be identified quickly and reliably. Considering the high value of energy and cabin real estate aboard the ISS, the sensor should be economical with volume and energy consumption. Optical sensors do not fulfil this criteria, being themselves bulky and expensive. Ideally, sensors should also have a long lifespan and be durable, which contributes towards a low cost factor as fewer repairs need to be done. Potentiometric gas sensors may not fully satisfy the durability requirement, as some glass components are fragile. Replacement parts would also involve sending new equipment from Earth, but space cargo is very precious. The cost per pound of cargo aboard SpaceX carriers that supply the ISS is ~ $27,000. So what are the solutions to these challenges?

2.2 Carbon Nanotube Based Gas Sensors

NASA has an In-Space Manufacturing (ISM) Initiative to develop 'on demand fabrication, repair and recycling capabilities' on board the ISS as well as on future spacecraft missions to farther out in the solar system. The ISM motto is *'Make it, Don't Take it'*. What if we can develop gas sensors for ISM, making them more sustainable for missions?

At the Center for Nanotechnology at NASA Ames, this issue is being addressed via the development of gas sensors with nanotubes as the active sensing material. These nanotubes can be dispersed in liquid to form an ink medium that can be deposited or 'printed' onto electrode substrates.

Dr Beomseok Kim, my direct supervisor at NASA Ames, has developed a nanotube based gas sensor using single-walled carbon nanotubes (SWCNT) deposited onto electrode channels on a printed circuit board (PCB). The SWCNTs in raw form are shown in the Transmission Electron Microscope image in Figure 3, which are 10,000 smaller in diameter than the average human hair. These nanotubes are treated with acid to functionalize them with carboxyl groups (-COOH).The resulting SWCNT-COOH is deposited onto the PCB, with nanotubes forming bridges between electrodes as shown in Figure 4. This creates a chemiresistive gas sensor, whereby the resistance of the electrode channel can be varied by the interaction of gas molecules with the nanotube material.The sensor signal is a measurement of the change in resistance.

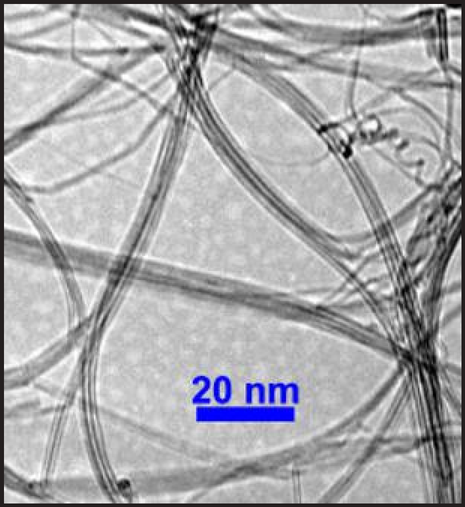


Figure 3: TEM image of the Single-Walled Nanotubes used to make the gas sensors. Source: Nanostructured & Amorphous Materials Inc., Houston, TX

In addition to the SWCNT-COOH, acid and base were used to create a spectrum of various pH channels on the PCB, as illustrated in Figure 5b. This sensor was then exposed to variable part per million (ppm) gas concentrations of CO_2 or NH_3 with controlled relative humidity at 62% to mimic ISS conditions.

Empirical results show that the sensor response to NH_3 is amplified and positive in acid pre-conditioned channels whilst the response to CO_2 is amplified and negative in basic pre-conditioned channels. This is summarized in Figure 6. Also noticeable is that the magnitude of sensor response increases as gas concentration increases. Figure 7 depicts the selectivity of the sensor response to NH_3 and CO_2 at pH 1.9 and pH 9.1 respectively.

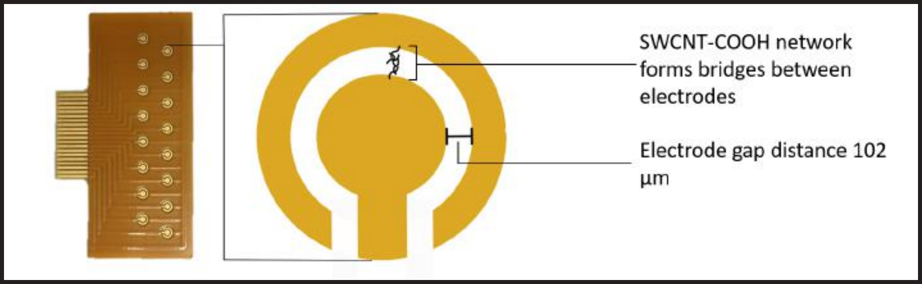
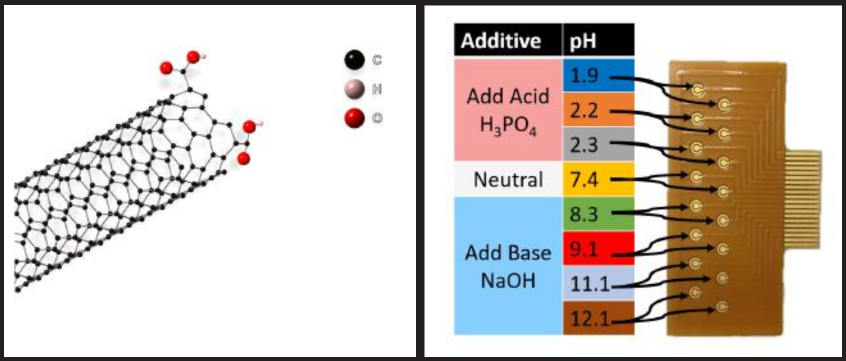


Figure 4: Image of the Printed Circuit Board Sensor with an illustration of an electrode channel, showing that deposited nanotubes form bridges between the electrode gap. From Kim *et al.* 2019.



Additive	pH
Add Acid H_3PO_4	1.9
	2.2
	2.3
Neutral	7.4
Add Base NaOH	8.3
	9.1
	11.1
	12.1

(a) (b)

Figure 5: (a) Illustration of a Carboxylated Single Walled Carbon Nanotube (SWCNT-COOH) with two carboxyl groups attached. (b) Additive acid and base used to create various pH channels on the sensor. SWCNT-COOH added to each channel.

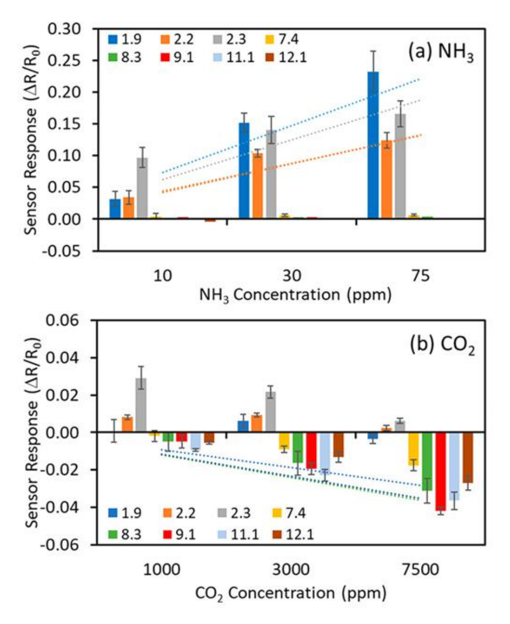


Figure 6: Sensor responses (ΔR/R0) of acid- or base-pretreated SWCNT–COOH samples to (a) NH_3 and (b) CO_2. Data for each bar is averaged from three different gas exposures. A positive NH_3 sensor response is higher in acid-preconditioned SWCNT–COOH. A negative CO_2 sensor response is highest in base-preconditioned SWCNT–COOH. Increasing the target gas concentration appears to increase the sensor response. From Kim *et al.* 2019.

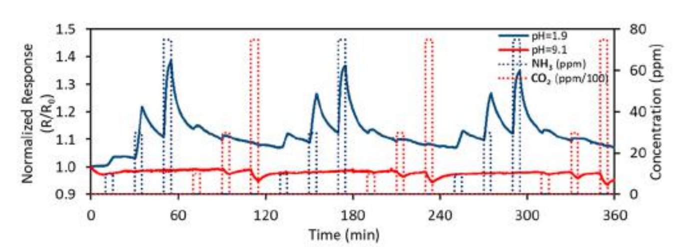


Figure 7: Normalized sensor response (R/R0) to NH_3 and CO_2 exposures using SWCNT–COOH at pH 1.9 (blue) and SWCNT–COOH at pH 9.1 (red). Exposed gas concentrations were 10, 30, and 75 ppm of NH_3 and 1000, 3000, and 7500 ppm of CO2 at 62%RH and 24°C. Relative gas concentrations indicated by the bar heights. Data was taken at 62%RH. From Kim *et al.* 2019.

2.2.1 Research Outcome

The acid-base interactions between gas and channel additive was proposed as the detection mechanism for the sensor. Instead of gas adsorption onto the SWCNT, it was postulated that gas molecules are dissolved in the high humidity aqueous environment of the nanotube, thereby affecting the pH of the solution. This pH change would then influence the carboxyl groups on the nanotube, causing either deprotonation or protonation. These events would consequently change the resistance of the nanotube, thereby manifesting as a sensor signal.

As the volume of water is too minute to probe with a pH meter to detect pH changes upon gas introduction, it was necessary to attempt computational modelling of the pH changes. This was my task during the internship. These python models aimed to do the following:

1. Associate gas concentration in ppm to dissolved concentration on the sensor channels
2. Determine pH changes when gases were introduced to a neutral solution
3. Determine pH changes when gases were introduced to an acidic/basic solution

The resulting models for NH_3 and CO_2 are shown in Figure 8. These models confirm that when adding a basic gas such as NH_3 to an acidic solution, the pH change within the same ppm range is larger compared to the pH change when the basic gas is introduced to a neutral solution. The same case is observed for adding an acidic gas such as CO_2 to a neutral vs basic solution. This amplified pH change can explain the increased magnitude in sensor signal when these acid-base reactions are implemented because the degree of protonation/deprotonation is enhanced. The models also suggest that the magnitude of pH change is also responsible for the observed relation between gas concentration and sensor response. Please see the publication for a more detailed description of this mechanism and the relevance of the carboxyl group pKa values.

The models were also extended to other toxic, acidic gases and basic amine gases to predict the feasibility of using this same sensor design to detect these gases:

- Hydrogen Sulphide
- Hydrogen Chloride
- Hydrogen Fluoride
- Methylamine
- Dimethylamine
- Trimethylamine

The models predict that the SWCNT-COOH sensor will be able to detect the Immediately Dangerous to Life and Health (IDLH) levels of all gases listed except Hydrogen Sulphide and Trimethylamine.

Improvements to the sensor were also suggested based on models that implemented stronger acids/bases as additives.

These additional modelling results, not shown in this report, are being investigated further for possible publication.

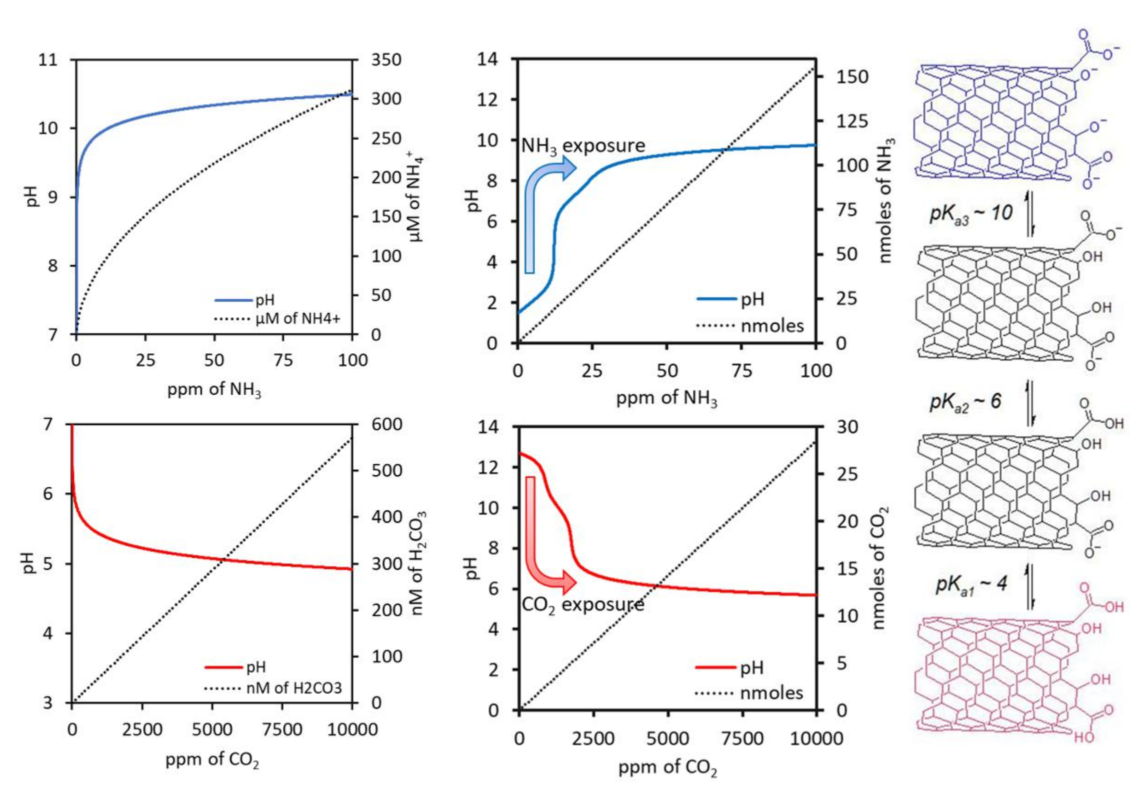


Figure 8: (**Left Graphs**) Calculated pH changes of water for given NH_3 concentration in ppm (blue line) and CO_2 concentration in ppm (red line). Dotted lines show ppm values of target gases tested and associated equilibrium concentration of $[NH_4^+]$ or $[H_2CO_3]$. (**Right Graphs**) (*top*) Computed titration to model the environment of the acid-preconditioned SWCNT–COOH sample. The dissolution of NH_3 to form NH_4^+ ions results in a significant pH increase in acidic solutions. (*bottom*) Computed titration to model the environment of base-preconditioned SWCNT–COOH samples. The dissolution of CO_2 to form H_2CO_3 results in a significant pH decrease in basic solution. (**Right Schematic**) Illustration of different degrees of protonation of edge carboxylic groups on SWCNTs induced by different pH environments. At high pH values above pKa $\approx$ 10, edge -COOH achieves the most deprotonation. At low pH values below pKa $\approx$ 4, edge -COOH achieves the most protonation. Adapted from Kim *et al.* 2019.

2.3 Deliverables

The requisite written output of the internship is summarized below, with both deliverables to NASA and NIHERST listed.

1. NASA deliverables
    - Preliminary Internship Plan
    - Poster

  - Final Student Report for Supervisor

2. NIHERST deliverables
  - Mid-internship Report-Read here
  - Final Report

My computational pH modeling work and description of the sensor mechanism also contributed towards a publication in ACS Applied Nanomaterials:

- Beomseok Kim, Thaddeus J. Norman, Ruth Sang Jones, Dong-il Moon, Jin-woo Han, and M. Meyyappan, *Carboxylated Single-Walled Carbon Nanotube Sensors with Varying pH for the Detection of Ammonia and Carbon Dioxide Using an Artificial Neural Network*, ACS Applied Nano Materials, DOI: 10.1021/acsanm.9b01401

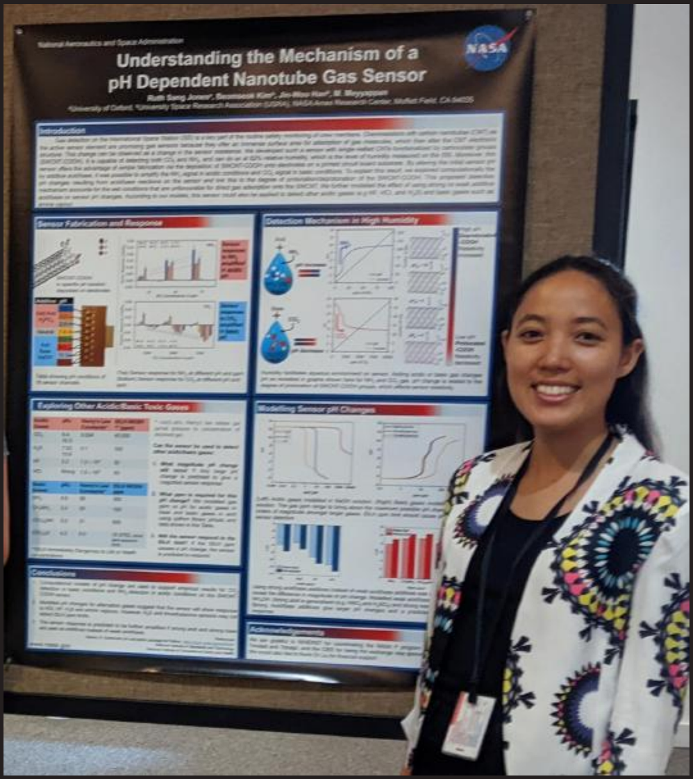


Figure 9: Presenting my poster at the NASA Ames Annual Summer Poster Symposium

2.4 Skills

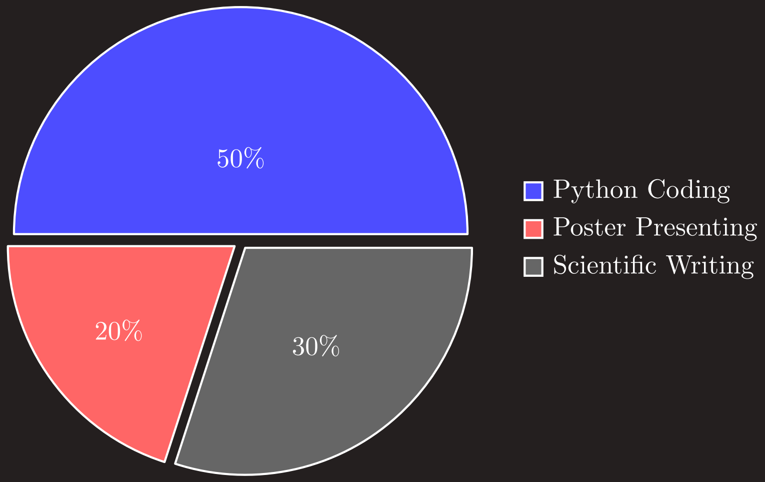


Figure 10: Estimation of time distributed to learning Transferable Skills

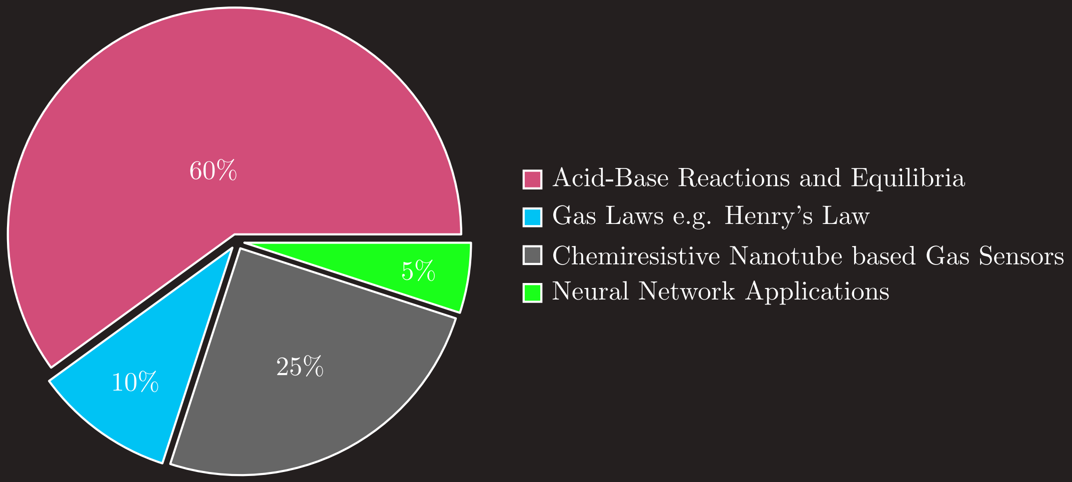


Figure 11: Estimation of time distributed to reading Theory & Literature

I have summarized here how I perceive my time was spent learning skills and acquiring new knowledge. My contribution to the research project was mainly computational, so learning and applying python was my primary activity.

Nevertheless, I had to understand the chemical processes occurring in the aqueous sensor environment in order to accurately construct models involving reactions between target gases and sensor material. My grasp of theory facilitated my communication of the research in multiple media formats. I designed and created content for my own poster and also contributed scientific writing towards a publication in a peer-reviewed academic journal. These coding and science communication skills are very valuable and transferable.

3 Impact

3.1 Scientific Impact

This work is a successful step towards achieving the In-Space Manufacturing goals set by NASA. Later versions of Dr Kim's gas sensor could one day be printed on board the ISS.

On a more technical side, the developed sensor is one of only a few to exhibit the application of carbon nanotubes to detect CO_2. The results also show very promising evidence that neural networks and machine learning can be very powerful in converting sensor signals to accurate gas concentrations.

The discussed mechanism of gas detection is also novel and opens a new avenue for research into how pH conditions can be leveraged to manufacture functional and effective carbon nanotube based sensors.

3.2 Development of Trinidad and Tobago

Whilst gas sensing on the ISS is an activity far away from home in T&T, there is definite relevance to its economical backbone- oil and natural gas. Gas sensors are very prevalent at industrial plants such as at oil and gas refineries.

But looking to the future and beyond the finite richness of our natural resources, we can turn to innovation to help develop T&T. As nanomaterials promise to disrupt multiple industries, including energy, medicine and electronics, should we start investing in nanomaterials and would it be feasible to begin nanomaterials manufacturing activities? Could we ever gain a competitive edge in this area? These are all questions that we can begin exploring.

And what about the commercial space industry that is growing rapidly? How can a small island nation find a niche in this area and in doing so create new jobs and diversify the job market.

I realise that I am posing more questions that delivering answers. But I just hope to bring to light the importance of investing in science, innovation and technology to secure the future of T&T.

4 Personal Reflections

I saw the opportunity to work on the nanotube sensor research as eye-opening because it revealed the applicability of nanomaterials to electronic devices, which is not always immediately tangible during my everyday, laboratory work back at Oxford. Finding out that I was responsible for computational modelling during my internship initially made me feel out of my comfort zone. But after about 5 weeks of acclimatizing, I was able to grasp the essential concepts necessary and recover and improve upon some of my python coding skills to construct the sensor pH change models. The project also involved the application of machine learning to convert the sensor signals to gas concentrations. This was not in my field, but I was invited to meet with the expert on this and asked questions to gain insight into the value of such work to this project and the wider field of sensors.

Figure 12: My supervisor (Dr Beomseok Kim) and I after our research group played Escape Room together.

The research environment at NASA ARC was incredibly amicable and my supervisor Dr Kim was immensely encouraging. The wider research group has a significant amount of research on-going into a variety of sensors, many intended to fit the In-Space Manufacturing objective. I was also able to take tours of several other research facilities at NASA ARC, including the Mars Roverscape, Fluid Mechanics Lab, Supercomputing facility and Vertical Gun Range. One of the highlight lectures that I attended was given by Dr James Green, NASA's Planetary Science Division Director, who spoke on the history of lunar exploration and introduced the upcoming and ambitious Artemis Project to send humans back to the moon in 2024. It was exhilarating to be in an environment where everyone is so keen about space.

I have always been inspired by NASA's trailblazing achievements. NASA embodies the collaborative spirit and curiosity of humanity and has always been to me a symbol of the vanguard. I realised that I manifested qualities of the organisation in myself whilst there, being eager and courageous to explore the unknown. This was relevant not just to my research, but to the people I met and the places I visited in California.

My positive perspective on NASA was reinforced when I saw its active efforts in giving so many undergraduate and graduate students research opportunities. I got to meet many of these very intelligent and motivated young people, whom I can now call friends.

I felt exceedingly proud of myself and my fellow Trinis for challenging ourselves to undertake this internship and to be young ambassadors for the country.

It was a truly confidence boosting experience and I have returned to Oxford with more drive to complete my DPhil and with hopes of becoming involved in the space industry for my future career.

Figure 13: Jumping into the future with Gabby and Becca, fellow interns at the Center for Nanomaterials.

Thank you for reading!