

14/10/19

• Overall tour of GPC lab

- Chemistry lab
- Ink Lab → Gas sensing equipment
- Chem. character. Lab → Dimatix inkjet printer
- S5100

• Classification of project goals

- Observation of all processes involved in gas sensing
 - 1) Ink synthesis (Hydrothermal process)
 - 2) Printing
 - 3) Ink characterizations (SEM/Raman ... etc)
 - 4) Sensor testing

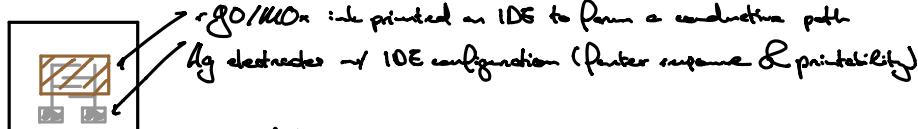
- Design & creation of my personal sensor

• Sensor optimization

- 1) Selectivity problem (humidity) using software (looking PCA)
- 2) Improvement / modification in hardware (new material/sensor structure configuration)

17/10/19

• Creation of a chemiresistive sensor w/ the following structure:



rGO/MnO_x ink printed on IDE to form a conductive path

Ag electrodes → 10E configuration (faster response & printability)

ND_x gas detection, gas interaction causing change in:

- Dielectric substrate a) Schottky barrier height for Mn_xSC at 100 Ω
(polymer film) b) Work function at conducting rGO

rGO interaction is rendered possible → presence of -CH groups, allowing H₊ bond formation. Gas detection leads to changes in R.I., V, and other electronic parameters.

18/10/19

• Printing process:

Replace cartridge, Set ink settings Prepare substrate, Setup printing process
change jet spitter ⇒ (Ag in most cases) ⇒ cleaned w/ IPA ⇒ (V modulation, nozzle selection) ⇒ Print
if required & plate setting IPA

Dimatix software carries offset prior to printing. Offset must be found using Si wafer chip.

21/10/19

• Ink synthesis process (rGO/TiO_x recipe) - 1st part:

Prepare rGO mixture w/ DI Sonicate for 30 min Prepare MnO_x mixture Mix the 2, sonicate
H₂O (5.625 mg of rGO & ⇒ for uniform distribution ⇒ TiO₂, IPA on a solvent ⇒ for another 20 min ⇒
11.25 mg of H₂O) & sodium acetate on a solvent

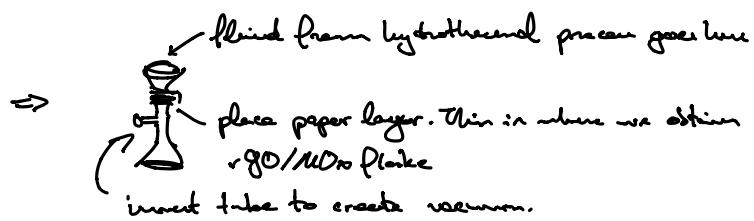
Prepare hydrothermal Hydrothermal process (Note: adequate cleaning w/ H₂O & IPA required
process chamber (tube ⇒ for 120°C at 8 bar. during the process)
placement of discs)

24/10/19

Ink synthesis process ($\text{rGO}/\text{Fe}_2\text{O}_3$) - 2nd part:

Vacuum filtration

- ↳ removal of undesired solvents & other chemicals
- ↳ Results in dry rGO/MnO_2 powder, used for characterization.



25/10/19

Characterisation (SEM):

Use of N2 gas to ensure no particles fall from the plate.
which can damage the equipment, use of C-tape

Moving process:
check the order of
mount & unmount
if required

Descending process, from
bottom & let it decompose
to remove the sample from
the machine

Supervisor presence in
mandatory.

28/10/19

Independent ink synthesis: Fe_2O_3 . following prev. experience Cu_2O . same MnO_2 . follow recipe

$\text{rGO}/\text{Cu}_2\text{O}$:

20ml DI H_2O + 7.5mg rGO &	\Rightarrow rGO mixture sonicated for 30 mins.	10ml of 68mM NaOH in
5ml DI H_2O + 18.3mg $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	\Rightarrow $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ solution added then sonicated for 2 hours	\Rightarrow DI H_2O added dropwise, left → to stir for a further 2 hours

Hydrothermal process for
60°C & 2 hours, added
IPA & glucose, boiled at
100°C for 5 hours

Mixed after vacuum filtration,
with IPA & 2-butanone to form
binder free $\text{rGO}/\text{Cu}_2\text{O}$ ink

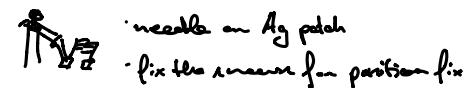
31/10/19

Procedures involved in working with gas sensing instrument:

- ↳ Value of the gas tank must be carefully handled, be sure to select the right valve
- ↳ Proper connection must be made between sensor & machine
- ↳ Must check air flow to make sure the tank containing gas sensor is well sealed ← Use of MS Access

Gases available: NO_2 , NH_3 , CO_2 , and $\text{H}_2\text{O(g)}$

C humidity needs to be fixed



4/11/19

Ink testing prior to printing if an electrode:

1) Drop casting: droplets of rGO/MnO_2 on ITO section

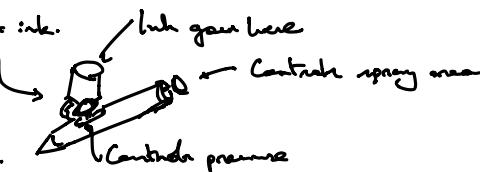
2) Spray casting: use an airburst to cast ITO section w/ rGO/MnO_2 ink.

Both require heating afterwards to obtain accurate R values of the conductive paths, this is the base R of the sensor.

Make sure that the ink is applied only to the ITO section of the sensor.

Prepare cleaning wipe/glass sheet to prevent ink going to non-target areas.

↳ Drop casting: Overload in Keithley, dry spray casting later ($\text{rGO}/\text{Fe}_2\text{O}_3$ ink used)



7/11/19

- Spray coating result: several hundred of $\mu\Omega$, conductive path is formed (albeit weak). Try different hydrothermal parameters, testing w/ Cu_2O also necessary. R value too high atm to be put into gas sensing instrument.

8/11/19

- $\text{rGO/Cu}_2\text{O}$ is tested. Drop casting gives unclear response, but spray casting provides stable results in the range of hundreds of $\mu\Omega$ & good enough to be tested.

13/11/19

- Meeting w/ Tomfique: need to think about the directions I want to take on the project. Dimension of what I've done so far, going over my theoretical background.

- Idea so far: increasing sensitivity through addition of extra hydroxyl group. 3D rearrangement of rGO/MOs ink which may prevent H_2O interaction to occur? Modification of bare R of the gas sensor by study its effect on sensor performance. Injection of longer signal to cause Joule heating & accelerating desorption/desorption of sensing materials. Selectivity optimization is another option, use of PCA: any way to implement ML techniques to PCA?

14/11/19

- Test gas sensing data obtained, use Oxyg's custom cycle: testing NO_2 exposure gradual decrease from 100 ppm to 20 ppm w/ 20 ppm decrease every cycle. IV kept constant through entire process.

15/11/19

- Mock presentation: take care at the jargons, more attention towards the graph explanation: concepts such as baseline drift must be elaborated w.r.t. response/recovery speed. Change the presentation template to match with the department. TIME TOO SHORT! Practice more to match 10 mins ppt. time.

18/11/19

- Presentation feedback: failure of explaining sensor-analyte interaction mechanism, will need to do sanity check with Oxyg. Presentation itself might have decent but requires more lit. review.

21/11/19

- Further testing w/ $\text{rGO/Cu}_2\text{O}$ sensor. SEM observation of Cu_2O ink & Fe_2O_3 , observation & comparison of the et structure and surface topology.

25/11/19

- Discussion on direction of the project. Take a "bottom-up" approach:

↳ test how modifying base resistance can affect sensor response & baseline drift. Modification made possible potentially through controlling MOx concentration & duration of hydrothermal process & addition of Ag nanoparticles to the ink.

↳ test how input I can affect sensor performance & easier to test, verify whether this is possible. Selectivity improvement through software will be attempted if time allows.

- Initial experiments using $\text{rGO/Cu}_2\text{O}$ sensor on increasing I & note that machine cannot control I, so increase V.

28/11/19

- Increased ν application during recovery to accelerate desorption: 1V at dry air & NO_x exposure stage, increase V at the purge stage to 2V, 3V ... 10V.
- 20V initially experimented, return overflow error from Keithley ↳ may be problematic as we are unable to use high enough voltage to induce self heating.

29/11/19

- Continued experiments on testing increased voltage on sensor. Tried up to 10V. Data obtained from 4V-5V, 10V-7.5V, and 1-10V. Confirmed slight increase in sensor recovery speed visible from R value shown on sensing device ($\approx 20k\Omega$ for V increase of 2.5V)
- Preparation for 2nd industrial meeting.

2/12/19

- Feedback from meeting: Observation of response change by V modification: Parikh's antenna, could be used for baseline drift removal
 - a) Think of different ways of applying V : pulses is a good idea, check whether this is possible from the machine AC waves or triangular waves? Look to improve both baseline drift & consumption of the device.
 - b) Creation of a repeatable V operation cycle
 - c) Possibly look for PCA technique for selectivity if time allows
 - d) Reading literature to confirm whether this was previously attempted. Use Monday.

14/12/19

- PCA look-up:
 - ↳ Possible ML methods: specific patterning according to a type of sensor/analyte, is ML training possible from a whole graph result? Potentially works like image recognition.
 - ↳ Use of classifiers for prediction region creation? Maybe look for ways to achieve this in real-time?

20/12/19

- Process excel data from lab S-value calculation. Increased V value unfortunately does not show drastic improvement.

25/12/19

- Began TMR

16/1/20

- Continued voltage testing. As V increase often leads to machine failure, look for alternate ways to test the effect of V on the sensor.
 - ↳ Increase base R of the sensor, so that even w/ high V values, I stay low preventing Keithley overflow ↳ use another sensor/modify concentration
 - ↳ May be solved if high V value is run with smaller values
- Lookup PCA in case the experiment fails in a backup.
- ↳ Python for data processing & Java for user interface? Go-ap and Oxy.

17/1/20

- Switch to rGO/CuO_x (2nd) route:
 - ↳ few research, good for testing
- 20 mL DI H₂O + 22 mg GO, Addition of 2 mL ammonia for 1 hour for ↓ NH₃(aq). nanocubes → source, transfer to => for 8 h at 180°C longer separation for another 1 h. taller
- Similar method can be used for rGO/Cu₂O, multi-step where addition of Copper source taken place during introduction of cobalt source.

21/1/20

- Testing new ink, go through drop casting to spray coating, resistance value variation from 10Ω down to tens of kΩ depending on MOx amount, allows wider option for testing.

23/1/20

- Further testing with CuO_x. Go through the same procedure used for rGO/CuO. Process detail kept in machine

24/1/20

- PCA tutorial completed. use of online resources to go through the processes involved. Look whether ML application is possible on the PCA result produced as scatter plot. Other challenges:
 - ↳ Code on how to use offline .CSV file from local storage
 - ↳ User interaction? User inputs your sensing result and the program predicts what type of analyte it is.

28/1/20

- Further testing with CuO_x: then there expose the sensor to a saturated state. Find if this brings any changes to the sensing result.

30/1/20

- Continue testing. Keep voltage variation between 0V - 10V.

3/2/20

- Potential for new direction on the research: use of hydrophobic MoS₂ & rGO/MoO_x ink for sensor. The hydrophobic property may allow independence from error caused by presence of humidity. See Orey's email for the reference paper. Wait for materials to arrive. Raman test was attempted but machine X functioning & went ruined to do it.

6/2/20

- Application of classifiers on PCA. Successful implementation of standard classifiers such as Gaussian NB & Logistic regression. Tested using a fake data created using CSV file. 3 random parameters used, achieved reduction of dimension to 2D.

7/2/20

• Testing using MoSe: prepare 5 samples w/ diff % of rGO/CuO & MoSe, label A to E:

A: Pure MoSe

B: 25% rGO/CuO (2ml) + 75% MoSe

C: Half

D: 75% rGO/CuO + 25% MoSe

E: Pure rGO/CuO

Solutions prepared to be tested on Monday.

10/2/20

A: 49.5° C: 91.4° E: 24.69° ← B data outlier, MoSe presence is not hydrophobic enough to have a significant effect on advancing humidity independence (contact angle $> 90^\circ$).
B: 19.3° (?) D: 32.88°

11/2/20

• Data recovery using origin: Voltage increment $1V \rightarrow 10V$ applied on CuO, confirmed effect of V on sensor performance, w/ increase in gradient amplitude due to higher V, inc. from 7.14 to 8.79 . However, effect too small considering voltage increase.
Additional problem identified are:

↳ Jumps in $\frac{V_0}{2}$ & $\frac{A_1}{2}$ values when higher V is applied: unknown mechanism

↳ Voltage value variation in the machine requires at least one minute for new V value ← software fix/ask the manufacturer

12/2/20

• Meeting w/ Tamara, Fassbacht:

↳ V too long to be considered a pulse. Either: fix the machine by contacting the manufacturer $\exists \underline{\text{ADAP}}$ by using V sweep mode

• Doubt on MoSe hydrophobic ink, contact angle not high enough

• PCA result seems positive, must be tested on real values.

18/2/20

• MoSe experiment attempted once again, this time using spray coating to ensure level amount is applied on the surface. Test failure, w/ A-E solutions showing arbitrary values between $10-30^\circ$, discord experiment.

21/2/20

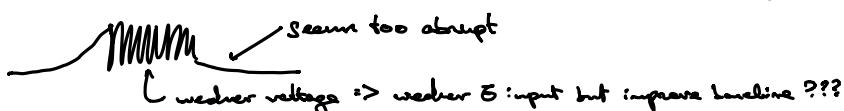
• Exploration of Vsweep mode in the instrument: seemingly able to reduce baseline drift, sweep mode allows manipulation of:

→ V_{max}

→ V_{min}

→ Change of V per second ← for fastest peak possible, assume that this value is equal to $V_{max} - V_{min}$.

• Only need cont. 2V for initial dry air to expand, 2V - 1.65V for purge, followed by another 2V DC for purge: because add air we reduce input V yet baseline is reduced. The graph shows the following result:



Requires further testing, at this stage plan to get as many data as possible & focus on PCA while waiting for data.

24/2/20

- Continued voltage sweep testing, using wedge amplitude pulses: 2-1.6V, 2-1.8V... etc, now testing for repeatability.

25/2/20

- Continued testing, more complex conditions such as variation in duration of V_{sweep} and so on, test for repeatability.

27/2/20

- Major issue found w/ the machine. Repeatability poor shown:



← Transition between V_{sweep} & DC current.

DC voltage of 2V normally, yet significantly different curve position.

- Tested w/ another V_{sweep} amplitude:



Graph shows DC value is equal to final V value of sweep stage, instead of the designated V_{set} . Confirmed w/ excel

- Recovery X achieved, test again w/ increasing V.

28/2/20

- Prepared for a new voltage release, test for V_{sweep} continued over entirety of gamma cycle:



- Test for 2V-3V and others.

3/3/20

- Continued testing for V_{sweep} . Begin collecting data for the final report (SEM images, Raman - needs to be done, rheology data for rGO/CuOx test).

5/3/20

- Continued testing for V_{sweep} . The problem of transition from DC \rightarrow V_{sweep} still exists. Consult Ong on this matter.

9/3/20

- Testing for V_{sweep}

10/3/20

- Testing for V_{sweep} , prep for meeting. V_{sweep} overall shows an improvement in terms of baseline drift. Final report template to be created.

11/3/20

- Meeting feedback: - discuss baseline drift, focus on PCA w/ application of real data.

- focus on PCA of data from rGO/CuOx and rGO/CuCoO_x, which will be tested w/ gamma exposure in dry

condition & met condition during winter break. * Failed due to Covid-19

3/4/20

Meeting w/ Tomfige online: - retrieve data (what's available from Oxyg.)

- think about what I can do during this time

⇒ PCA, optimizing the code, or for the Pdmg data use pseudo-random number generator?

Fixing parameters for PCA: Max S. Area of recovery, response ratio, exp. time? dimension w/ Oxyg.

C Volume has similar size for PCA

9/4/20

Data received, modified to get the 3 parameters: unfortunately data for only Co₃O₄ & CuCoO is available, and the test w/ gas in dry vs H₂O was done w/ only CuCoO & choose this answer. Note the gas is mixed NH₃ & NO₂.

10/4/20

Feedback: general direction ok, creating pseudo-random data seems fine, maybe implement something to allow prediction? Testing unknown humidity based on PCA result?

The fact that it is mixed gas (NO₂ & NH₃) can overcomplicate things.

16/4/20

10% to 90% of max S.

Parameters Max S, A ratio. Resp time ↗ recovered from data dump, applied on PCA, able to show distinct regions.

17/4/20

Positive PCA result, new test w/ random data. Tomfige: concerned that 3 parameters are not enough, look for more if pos

1/5/20

So far: - PCA code updated w/ explanation

- New graphs added using new classifiers, SVM & Random Forest

- Random data generator created

C Test PCA result w/ different std deviation settings:

1. $\sigma = 10\% \text{ of } \mu$

2. $\sigma = 1\% \text{ of } \mu$

3. $\sigma = 20\% \text{ of } \mu$

4. $\sigma = 50\% \text{ of } \mu$

5. $\sigma = 15\% \text{ of } \mu$

6. $\sigma = 17.5\% \text{ of } \mu$, additional values will also be tested.

• Fixed PCA region issue where the color of dot on scatter point ≠ decision region

• Show PC percentage vals on the plot

• Report lit. review section in progress

* Most of the test data unable due to Covid-19, won't able to retrieve soon before moving back to S.K.

• More extensive lit. review for report.

6/5/20

Random data successful. Try to find largest σ value which allows acceptable accuracy. Took w/ graham's data (from Oxy) for $\text{rGO}/\text{Fe}_2\text{O}_3$ resistivity which has std deviation value which could be used for random data generation.

7/5/20

- New code w/ 6 features: New S. Rep.t., A. ratio, Recov. A & Res. A., gradient. Shows little to no difference due to the fact that the features are linked to the 3 original ones.
Optimal σ found to be approx $\sigma \approx 15\%$ of μ .

10/5/20

- Fit review: jumps potentially due to reduction of rGO from Voltage \Rightarrow higher conductivity? confirm w/ Oxy.
- Code optimization: added user input feature.

15/5/20

- Feedback:
 - Fit review might be wrong, further red. difficult due to rGO stability
 - put more detail on PCA
 - fluorescent to show workflow