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Detection Limits of Nanoparticle Sensors

Final Report

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Contract Scientific Authority: D. Pedersen, DRDC Suffield

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Final Report: Detection Limits of Nanoparticle Sensors – Summer Student

June-August 2009

Toby Bond, Robert W. J. Scott, University of Saskatchewan

Introduction

Our lab has been working over the past several months to test and characterize the stability and gas-sensing properties of Ag nanoparticle films deposited on substrates at DRDC. Early on, it became apparent that reproducibility as well as storage and testing conditions of the films were non-trivial considerations, however clear responses to hexane, ethanol, and water were demonstrated. However, due to the irreproducibility of responses, it was not possible to generate full detection limit studies for the response of the sensors to various gases. This report summarizes all of our findings between June and August 2009. Work in the lab was carried out by Toby Bond, a research technician in the Scott laboratory (300 hrs, roughly 100 hrs/month), while Prof. Robert Scott spent ca. 20 hrs/month over the three months on the project providing guidance and direction to the project; the latter was an in-kind contribution and was not billed.

Experimental

The supplied sensors (deposited on a glass slide with silver contacts) were mounted in a sealed gas flow cell using alligator clips (fig. 1c). These were soldered to wires which ran out of the cell and were connected to a Solartron SI 1287 electrochemical interface and an SI 1260 impedance/gain-phase analyzer. The concentration of analyte gas was controlled using 2 flow meters, a carrier gas cylinder, and a bubbler arranged as in Fig. 1a.

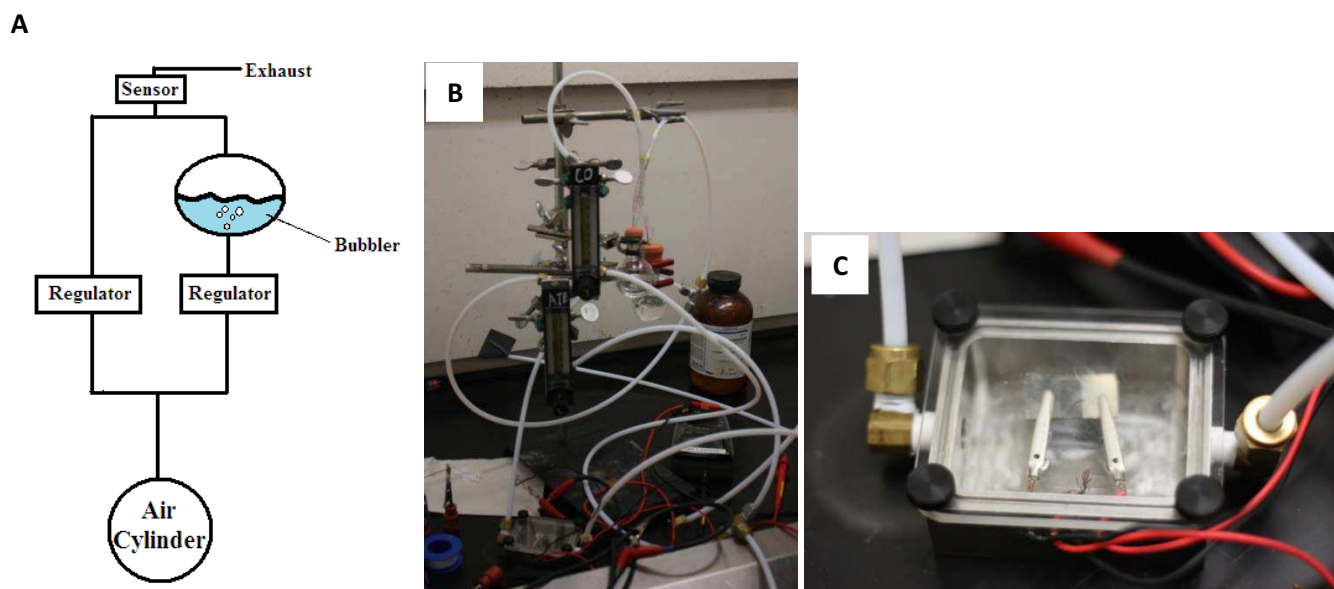


Fig. 1: a) Schematic of gas flow apparatus b) actual apparatus, including sensor cell and flow meters c) sample chamber

The analyte concentration is controlled by altering the ratio of flow rates between the clean channel and the bubbler channel while keeping the total flow rate constant. Actual concentrations can be calculated from the fraction of saturated flow and the vapour pressure of the analyte (P_v):

$$[\text{Analyte}] = P_v \frac{(\text{sat'd flow rate})}{(\text{sat'd flow rate}) + (\text{clean flow rate})}$$

Because it facilitates comparison between different analyte gases, results in this report are generally reported as a fraction of saturation. The saturation concentrations of hexane and ethanol are approximately 150 ppt and 60 ppt, respectively.

Storage conditions varied over the course of the project as a variety of conditions were used in an effort to stabilize baselines. These included, storing in a desiccator, inert gas, open air, vacuum, and under gas flow (air and inert gas). These are discussed throughout the report.

Initial results

Upon receiving the first batch of samples, the baseline signals were measured under air flow (using industrial-grade compressed air) at 1V. Comparing these with the baseline measurements provided, a twofold increase in baseline current was generally observed for all sensors during shipping (see Table 1). Baseline drift was observed for all the samples under air, and appeared to be linear over long periods of time (Fig. 2).

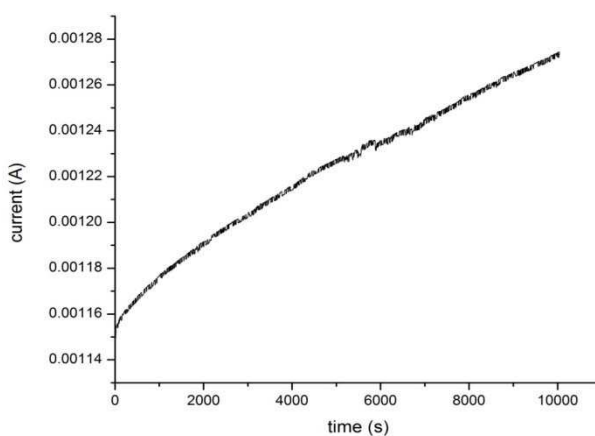


Fig. 2: Drifting baseline under industrial-grade air flow

For the first batch of six samples, Table 1 shows the changing currents over time. All currents are reported for a constant voltage of 1V, and all of the values reported are prior to any exposure to analyte gases. Samples were stored in a desiccator in air at room temperature.

Sensor	Before Shipping (mA)	After Shipping (mA) (June 19)	First measurement (mA)
1	1.4×10^{-4}	3.00×10^{-4}	2.95×10^{-4} (June 22)
2	1.4×10^{-6}	2.58×10^{-6}	2.17×10^{-6} (June 22)
3	2.2×10^{-4}	5.45×10^{-4}	2.51×10^{-4} (July 2)
4	1.0×10^{-7}	1.61×10^{-7}	1.93×10^{-8} (July 3)
5	1.0×10^{-7}	1.75×10^{-6}	7.04×10^{-9} (July 10)
6	7.6×10^{-8}	8.25×10^{-8}	1.46×10^{-8} (June 26)

Initial responses with hexane were measured using fully saturated vapour. These responses were very sharp, however they did not fully recover, were difficult to reproduce, and behaved unpredictably (such as sharp recovery when there was no change in analyte gas concentration, see Figure 3a and b).

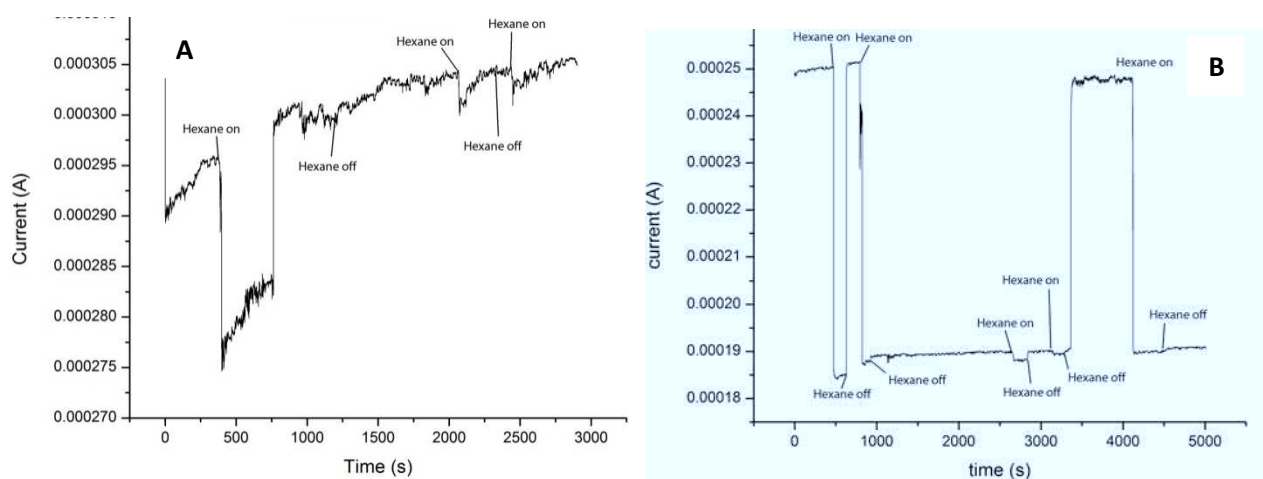


Fig. 3: a) Initial response to saturated hexane of Sensor #1 at 1V **b)** Response of Sensor #3 to saturated hexane @ 1V

This unstable behaviour was likely due to liquid formation on the film, so subsequent tests were performed at concentrations no more than ½-saturation, which gave much more reproducible results (Fig. 4a). The response appears to be proportional to concentration (Fig. 4b). **Given the rising baseline, it is very difficult to determine the detection limit of the sensor to hexane, but it is likely in the order of ca. 10 ppt.**

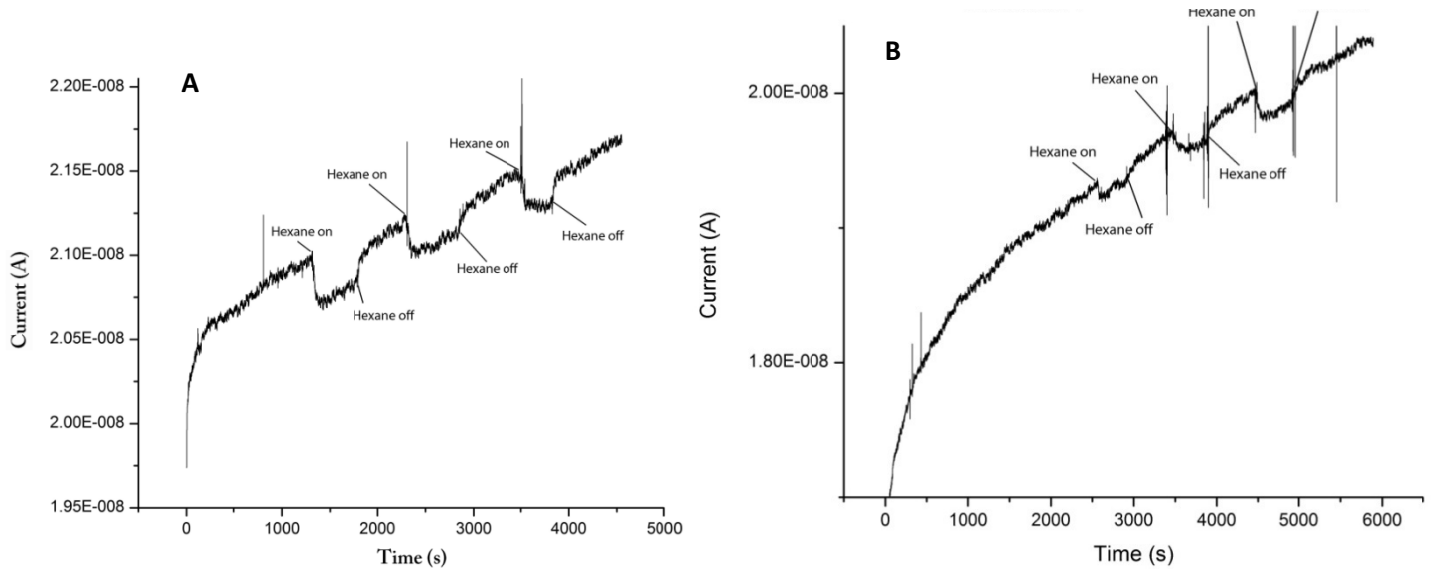


Fig. 4: a) Repeated injection of ½-saturated hexane using Sensor #4 @ 1V **b)** Response of same sensor to 75, 50- and 37.5 ppt hexane(in air), respectively.

The sensors also respond to ethanol vapour. Only one test was conducted, but the profile of the response (sharp response with gradual recovery) was similar (Fig. 5).

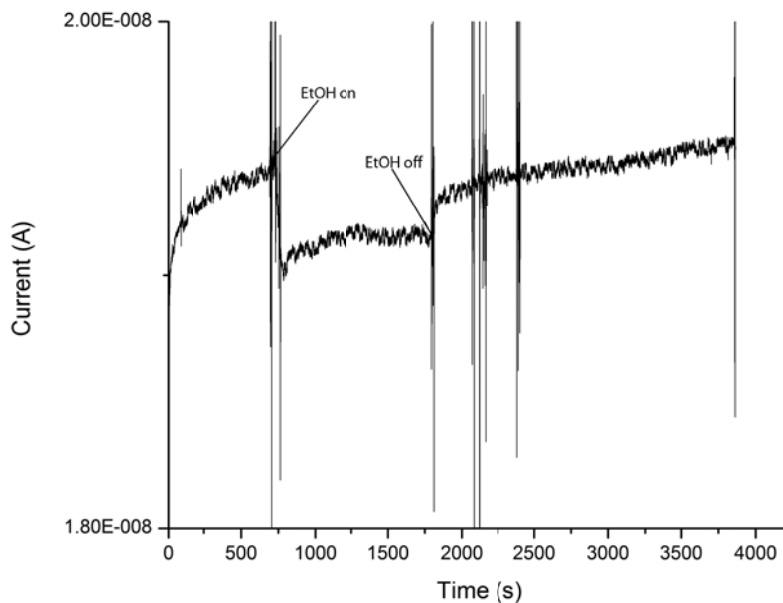


Fig. 5: Response of Sensor #4 to ethanol vapour @ 1V (1/2 saturation).

Storage Conditions and Cleaning

The first batch of sensors was stored under air in a desiccator with anhydrous calcium sulfate. Over 3-4 weeks, the sensors all gradually lost conductivity until no current at all was observed at 1V. As this progressed, sensitivity and the S/N ratio both became poor (as shown in Fig. 6).

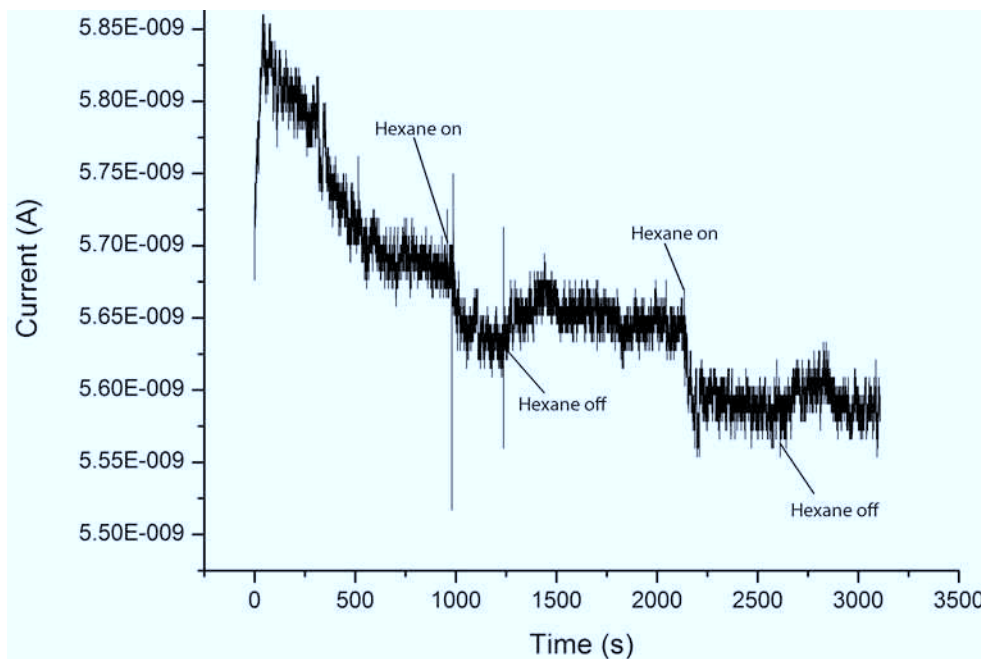


Fig. 6: Response of Sensor #6 to hexane after 4 weeks of storage in dry air.

This behaviour is consistent with oxidation of the film, as effective surface area would decrease and tunnelling currents across the film would be reduced due to larger dielectric barriers. The color of the film also changed during this time from blue (due to surface plasmon resonance) to brown (Fig. 7).

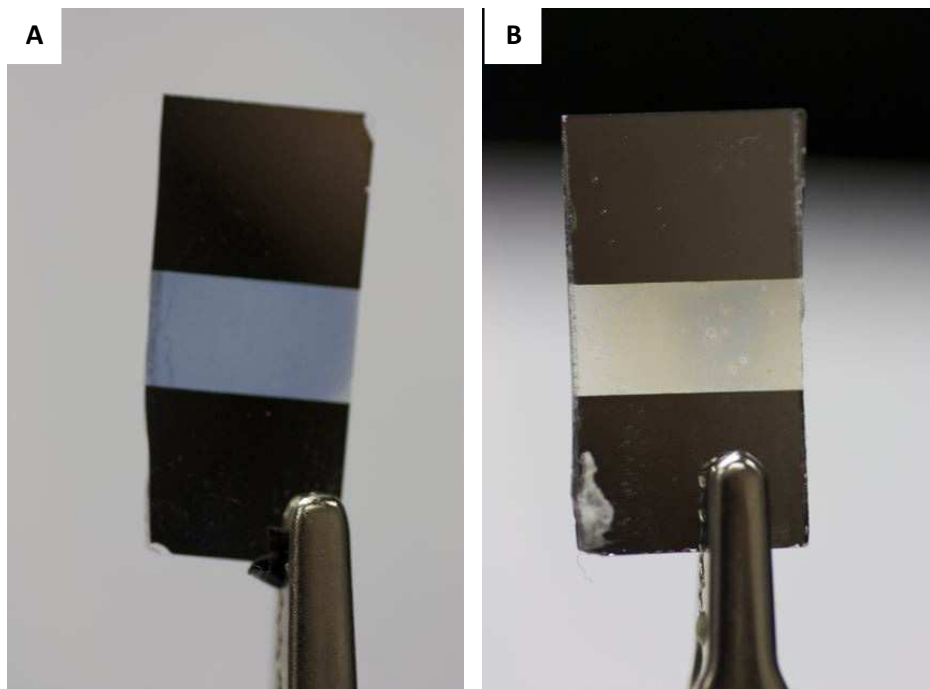


Fig. 7: a) A new sensor (#2 from the most recent batch) **b)** one of the sensors from the first batch after 2 months in air

In an attempt to reduce the sensors, three of them were placed under hydrogen gas flow over periods of 1-2 days. The sensors showed no conductivity before treatment, and none of them regained conductivity. Preliminary UV-Vis absorption studies were attempted to determine whether the sample conductivity and the SPR band could be recovered in the presence of H₂. These spectra were taken by taping the sample to a cuvette holder on a standard UV-Vis spectrometer. Results using this method were inconsistent and it became apparent that an apparatus that can maintain constant orientation and position of the film during *in-situ* gas exposure is likely required for conclusive UV-Vis spectroscopy studies.

Since many of the responses did not recover fully, or were not reproducible, efforts were made to remove analyte gas from the films and hopefully regain sensor response. The first method attempted was plasma cleaning, both with air plasma and argon plasma. Cleaning with air plasmas (for 10 seconds) removed the film from the slide entirely, as the substrate was transparent after cleaning and the current across the substrate dropped to zero. Cleaning with argon plasma (at low voltage for 10 seconds) produced a strange result: the baseline current went from 183 μA to 881 μA (possibly due to sintering) and the response to saturated hexane after cleaning was sharp and complete loss in signal, followed by an equally sharp recovery before clean air was re-injected (fig. 8).

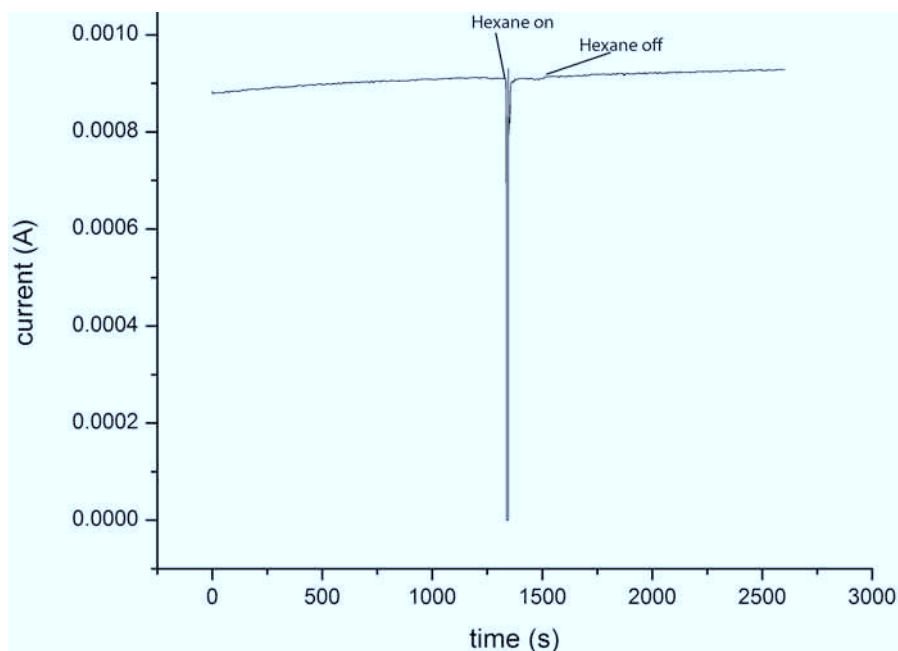


Fig. 8: Response of Sensor #1 to hexane after cleaning with argon plasma

Placing the sample under vacuum was also attempted by evacuating a flask containing a sensor, and by placing the sensor in a chamber that was hooked up to a continuously running pump. In both cases, the result was a loss of sensor function and a destabilization of the baseline current, even when exposed to vacuum for several hours. Discoloration and spotting were visible on the film after being placed under vacuum as well. It is unclear why this destabilization occurs, but it may be due to removal of analyte gas and/or water that is adsorbed onto the film, which could disrupt the film structure.

Placing the samples under air flow overnight to remove adsorbed gases resulted in complete loss of conductivity, however using a dry nitrogen flow resulted in a recovery of the baseline current. This was only tried on the last batch of sensors, and only with higher-particle-density samples, so flow generally had to be maintained for at least 12 hours and recovery did not always occur.

Recent Results

The second batch of sensors was stored in a desiccator with nitrogen atmosphere and P_2O_5 . It is not clear why, but all four sensors showed no response to hexane or ethanol using the same testing conditions as the first batch (industrial air, no more than $\frac{1}{2}$ -saturation, applied potential of 1 V). The sensors were kept in different storage conditions in an effort to regain sensor function, including vacuum, desiccator, air flow, and nitrogen flow, however all sensors showed complete loss of conductivity by the end of one week.

The third and final batch consisted of five sensors. Sensors 1, 2, and 3 had baselines in the milliamp range upon arrival, while sensors 4 and 5 had baselines of 10^{-5} and 10^{-7} , respectively. The last batch of sensors was stored in a large flask with no desiccant under an ultra-pure nitrogen gas atmosphere, except for one control sensor (sensor #5) which was stored in open air in the lab. After two days in open air, the baseline of the control sensor had dropped significantly, and was noisy and unpredictable. The color of the control sensor's film also changed over the first 10 days compared to a sensor that was stored under inert atmosphere (Fig. 9).

After two weeks, the control sensor was no longer conductive, whereas the sensor that was in inert atmosphere still had a baseline current of 0.344 mA (the same sensor pictured below).

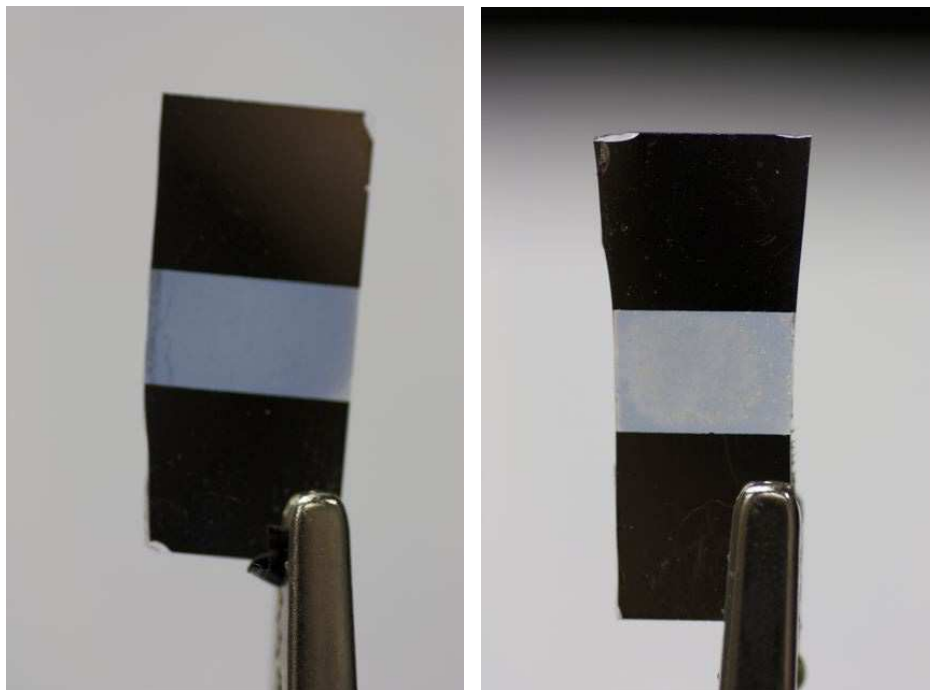


Fig. 9: a) Sensor #2 from most recent batch after 2 weeks under dry, inert atmosphere b) sensor #5, after 2 weeks in open air

Ultra-pure nitrogen was used as a carrier gas initially to prevent possible oxidation and eliminate moisture in the carrier gas as a possible source of noise. When the samples were placed under dry nitrogen flow, there was an initial positive drift in the signal, but after about an hour under flow this drift levelled off and the baseline became stable (Fig. 10).

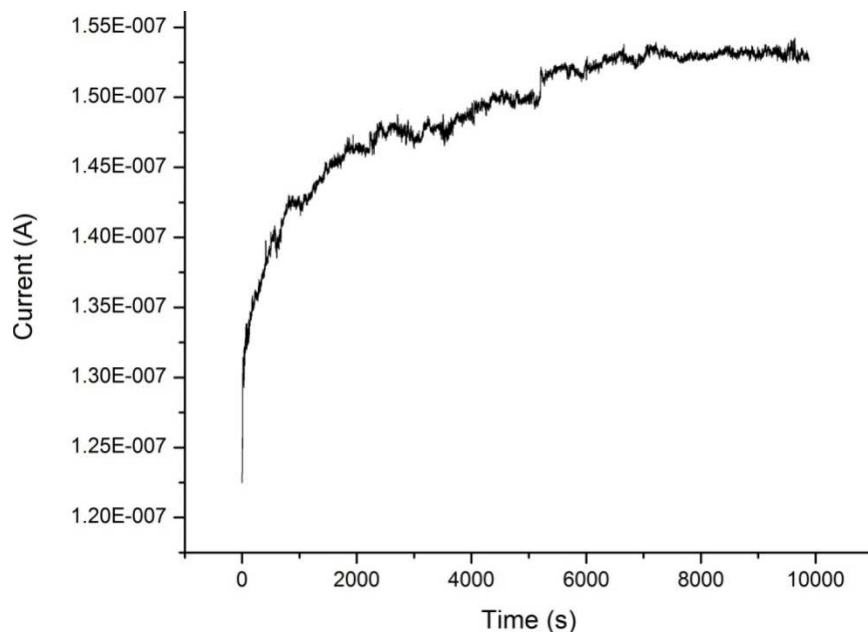


Fig. 10: Baseline of sensor #5 under ultra-pure nitrogen flow over 2 hours (directly after received)

We are uncertain why there is still positive drift for short time periods (control experiments verified that it was not due to electronic warming up, etc). However, given that a steady baseline is reached, it is very likely that the positive drift observed in previous samples was due to moisture (and/or oxygen) adsorption, as it was found that water vapour actually generates an increase in current (discussed below). Subsequent tests showed consistently stable baselines over long periods of time.

Sensors 4 and 5 were tested with both hexane and ethanol using ultra-pure nitrogen as the carrier gas, however no response at all was observed under N_2 . Sensor #2 was then tested with $\frac{1}{2}$ -saturated hexane using ultra-zero air as a carrier gas (@ 1 V). Hexane injection produced a sharp response from 3.83 mA to 3.50 mA under these conditions, however little to no recovery was observed upon hexane shutoff (Fig. 11).

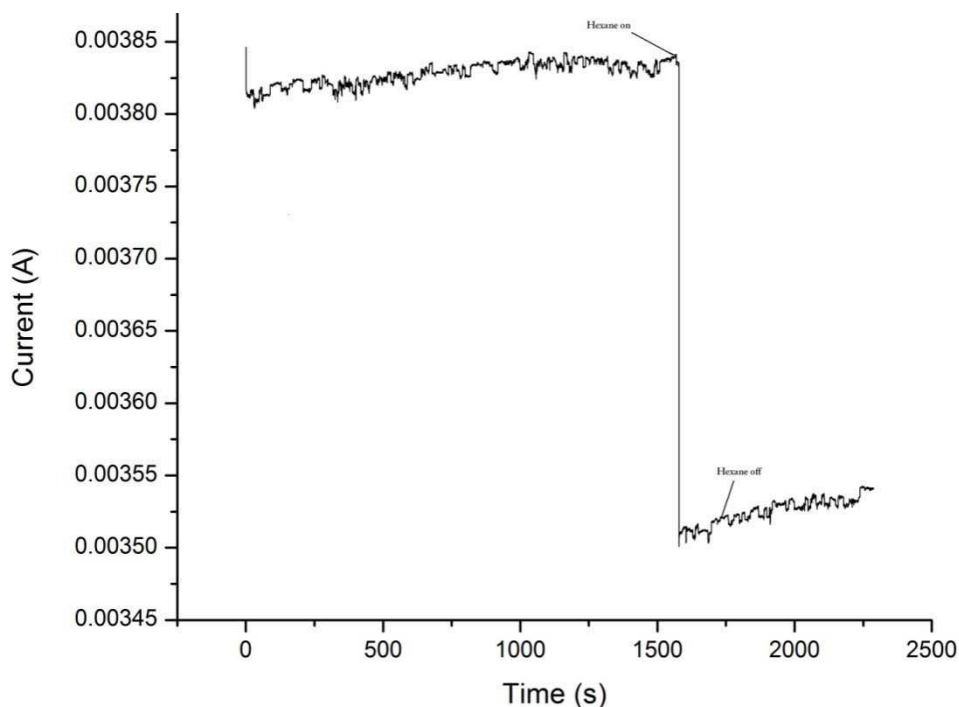


Fig. 11: Response of sensor #2 to hexane under ultra-zero air

It seems that the response to hexane requires the presence of oxygen, which indicates that the sensing mechanism is likely more complex than physical dielectric barrier formation of the adsorbed analyte. It is unclear at this point exactly what role oxygen might play in the sensing mechanism, but this is certainly a potential avenue of investigation. The sensor that showed this response (#2) did not show any further response to hexane (or water, which was also tested) after this initial result. Unfortunately, sensors 4 and 5 showed no responses to hexane in air after being exposed to hexane in nitrogen; attempts were made to remove adsorbed hexane but did not meet with any success.

The response to water vapour of sensor #3 was tested using $\frac{1}{2}$ -saturated water with ultra-zero air as a carrier gas at 1 V. This sensor had not been previously exposed to hexane or any other analytes. The response observed was actually a gradual, stepwise increase in current (from 2.97 mA to 3.31 mA). This was in contrast to the sharp drops in current observed with hexane and ethanol (Fig. 12).

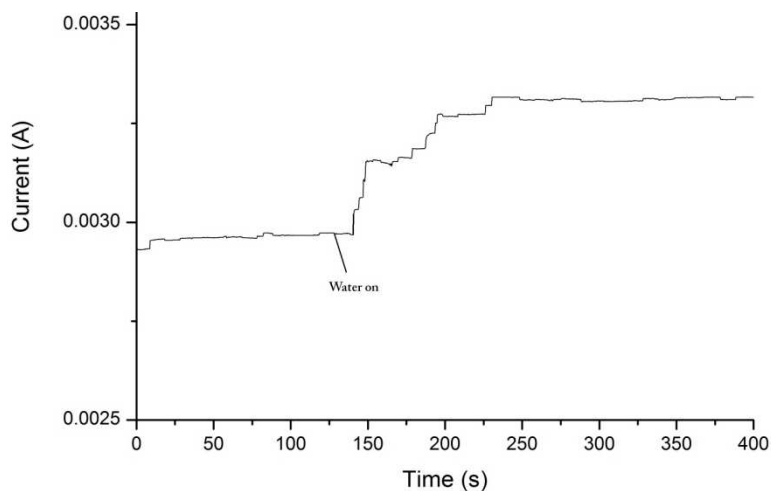


Fig. 12: Response of sensor #3 to water (scaled to show response)

It is not clear at this point why this kind of response is observed, but it certainly does indicate that the **previously observed drift in baseline is likely due to a gradual accumulation of moisture from the industrial grade air**. After this response, there was a sharp drop in current (far below the initial baseline) followed by noise (Fig. 13). This was likely due to liquid water formation on the substrate, and it subsided after 2 hours under nitrogen flow. The response was then reproduced 2 more times showing nearly the same sensitivity over the next 2 days.

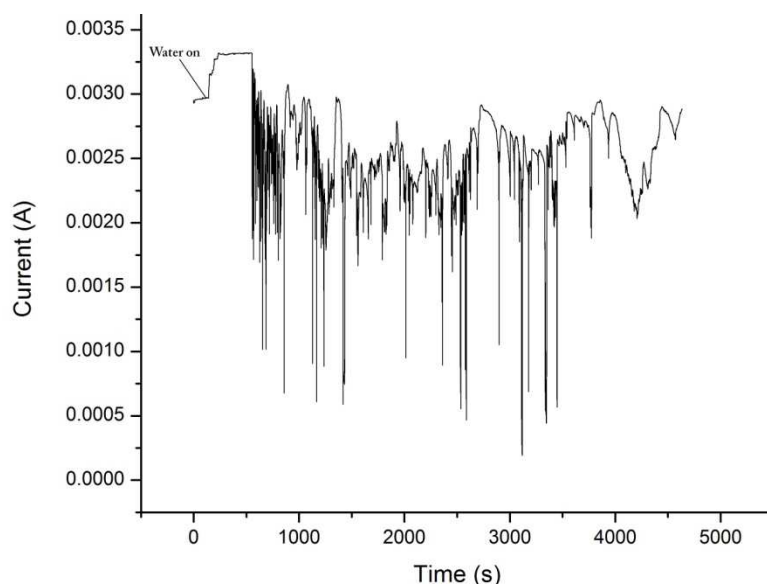


Fig. 13: Response of sensor #3 to water (including noise)

Because water gives a response opposite that of hexane and ethanol, it is possible that at least some of the drop in current for these responses is due to the displacement of adsorbed water on the surface. With the last batch tested, alternating injections of hexane and water were attempted, however no response was obtained. Further investigation is needed to determine the relationship between moisture and the hexane response, but it is at least evident that the samples must be thoroughly dried before characterizing the response to hexane more thoroughly.

Conclusions

Ag nanoparticle films have been shown to respond to the presence of hexane and ethanol vapour with a sharp drop in current, while the response to water is a gradual increase in current. These results appeared proportional to concentration of analyte gas, although reproducibility was a major problem. Moisture is likely the cause of the positive drift in signal initially observed when using industrial-grade compressed air. Low-particle-density films generally provided quicker recovery with more reproducible results. Finally, it should be noted that the presence of oxygen was required to generate a response to hexane; no response to hexanes was seen for sensors using nitrogen as a carrier gas.

The sensors are very sensitive to storage conditions, particularly to oxidation in open air. The best storage conditions at the moment appear to be simple inert atmosphere. Use of air plasmas and vacuum treatment appear to damage the sensor and destabilize baseline currents. Cleaning with argon plasma appears to sinter the film, but still appears to give some response (further investigation needed). Treatment of oxidized films with hydrogen gas has not yet succeeded in regaining conductivity for samples that show no signal, but may still be a method of re-reducing the films.

Future Work

Now that baselines have been stabilized, sensitivities can now be accurately measured and calibration and determination of detection limits should be possible with low-particle-density sensors. This is the highest priority. It is also important to determine the effect of moisture, oxygen, and increased testing potential on analyte response. The effect of analyte gas on the shape of I vs E plots is also of interest, as it may provide a way to differentiate between different analytes. Using a more volatile hydrocarbon such as pentane instead of hexane may also provide faster recoveries and better reproducibility. Response to other gases, such as acetone, methanol, etc. can also be characterized, as well as the effect of temperature on sensor response.

Further work on removal of adsorbed analyte from the films should also be performed: specifically, the use of low-level vacuum and argon cleaning. Reduction of oxidized samples with hydrogen gas should also be tried again with a conductive sample using an in-situ UV-Vis setup. Optical characterization of the films using atomic force microscopy and/or IR/UV-Vis absorption may also provide a way to quantify levels of analyte adsorption and film oxidation.

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The Scott Laboratory at the University of Saskatchewan has been working over the past several months to test and characterize the stability and gas sensing properties of Ag nanoparticle films deposited on substrates at DRDC Suffield. Early on, it became apparent that reproducibility as well as storage and testing conditions of these films were non-trivial considerations, however clear responses to hexane, ethanol, and water were demonstrated. However, due to the irreproducibility of responses, it was not possible to generate full detection limit studies for the response of the sensors to various gases. This report summarizes all of our findings between June and August 2009.

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