Chemical Detection by Impedance Spectroscopy of Along-Channel Admittance in Capacitively Coupled Vertically Aligned Carbon Nanotube Arrays

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Abstract
Vertically Aligned Carbon Nanotube Arrays (VANTAs) are found to support simultaneous sensing and discrimination of multiple types of chemical species. It is observed that applying a capacitive coupling to the top and bottom of the VANTA architecture provides a device that supports chemical sensing via electrical impedance measurement and that diverse species provide distinctive signal outputs as a function of measurement parameters. It is considered that this may provide a basis for a new type of electronic nose architecture.

Introduction
Chemical sensing is important to a wide variety of applications including environmental monitoring [1], food manufacturing [2], chemical processing, medical testing [3], and more. In previous generations, these have typically been confined mostly to single- or few-compound sensors. However, the ability to assess the chemical makeup of complex environments is becoming more important as it now becomes routine to have sufficient computational power to assess and react to complex chemical situations such as are found both in the day to day world and various industrial settings. Various electronic nose type technologies have been developed to address this growing need and opportunity. These typically take the form of linked arrays of individual sensing elements, including conductive polymer sensors, metal-oxide-semiconductor, surface acoustic wave sensors, and more [4] [5] [6] [7]. However, these designs have yet to become significantly used as they are prone to a number of drawbacks such as drift, loss of sensitivity in the presence of high concentrations of a single component, and difficulties in achieving absolute calibration [8].

Carbon nanotubes (CNTs) have been well-documented in the literature for their ability to provide chemical sensing capabilities [9] [10]. Their high surface-to-volume ratio combined with their chemically robust surface and electronic conductivity provides an ideal combination for serving as a robust chemical sensing element. Furthermore, previous studies have shown that rich sensing data can be collected from the impedance spectrum of a CNT sensor device [11] and frequency-based interrogation [12]. Previous CNT sensor designs have commonly used either single-CNT or a small number of parallelized CNTs across a pair of closely spaced electrodes [13] or have used a percolated network of CNTs spanning between interdigitated electrode arrays [14]. It is typically found that these different types of designs can commonly deliver disparate sensing responses due to fundamental differences in the sensing process. Where the sensors which are spanned by individual, defective CNTs provide a signal based upon chemical action on the electrical conductivity primarily of the individual tube itself (and often the junction with the contacting electrodes) whereas percolated CNT networks often produce a signal which is dominated by chemically-induced alterations in the conductivity the contact points between the CNTs [15].

VANTA has previously been described in the literature for constructing various electrical devices including supercapacitors [16] [17] and cathodes [18]. A capacitively coupled
VANTA as illustrated in figure 1A was conceived as a means for providing a sensing architecture which is distinct to these previous designs and provides a system in which the influence of the relevant chemistry on the electrical impedance may be measured along millions of CNTs simultaneously apart from effects from CNT-metal contacts or CNT-CNT contacts. Specifically, it is considered that by measuring both real and imaginary parts of the impedance under conditions of different applied frequency and voltage inputs that the VANTA array may be able to transduce the presence and identity of various chemical compounds.

**Objective**

Determine if a capacitively coupled VANTA is effective at sensing chemical and discriminating various chemical compounds when measured via impedance spectroscopy with various applied frequency and voltage inputs.
H$_2$O – Baseline : Nyquist

-Δ Imaginary Z(Ω)

Δ Real Z(Ω)

-4E+06 -3E+06 -2E+06 -1E+06 0E+00

0E+00 1E+06 2E+06

■ 0.01 V

○ 0.05 V

▲ 0.1 V

▼ 0.5 V

◆ 1.0 V

▲ 2.0 V
EtOH – Baseline : Nyquist

Δ Real (Ω)

Δ Imaginary(Ω)

0.01 V
0.05 V
0.1 V
0.5 V
1.0 V
2.0 V
Toluene – Baseline: Nyquist

\[ \Delta \text{Real } Z(\Omega) \]

-3.5E+06
-3.0E+06
-2.5E+06
-2.0E+06
-1.5E+06
-1.0E+06
-5.0E+05
0.0E+00
5.0E+05
-1E+06 0E+00 1E+06 2E+06 3E+06 4E+06 5E+06 6E+06

\[
\begin{array}{c}
\text{0.01 V} \\
\text{0.05 V} \\
\text{0.1 V} \\
\text{0.5 V} \\
\text{1.0 V} \\
\text{2.0 V} \\
\end{array}
\]
Figure Legend

Figure 1.

(A) The panel illustrates the basic design of the VANTA sensor construction and an SEM image of a VANTA array architecture.

(B) The panel shows a Nyquist-Bode plot of the measured sensor impedance under exposure to flowing N\textsubscript{2} prior to exposure to water vapor.

(C) The panel shows a Nyquist-Bode plot of the measured sensor impedance during exposure to water vapor.

(D) The panel shows a Nyquist plot of the difference signal of the measured sensor impedance during exposure of water vapor versus the baseline signal. This plot represents the complex plane projection that results from the data in panel (B) subtracted from the data in panel (C).

(E) The panel shows a Nyquist plot of the difference signal of the measured sensor impedance during exposure of ethanol vapor versus the baseline signal.

(F) The panel shows a Nyquist plot of the difference signal of the measured sensor impedance during exposure of toluene vapor versus the baseline signal.

(G) The panel shows a Nyquist plot of the difference signal of the measured sensor impedance during exposure of ethyl acetate vapor versus the baseline signal.
Results & Discussion

The impedance data of a device exposed only to dry N₂ provides a 'baseline' for the device electrical properties without exposure to other chemical environments as plotted as a Bode-Nyquist diagram as shown in figure (1B). The native device exhibits a single arc at frequencies between approximately 100 Hz and 100 kHz which is qualitatively characteristic of these devices exhibiting behavior as an effective circuit with capacitive and resistive behaviors acting in parallel. Furthermore, it is seen that different arc geometries are observed at different applied voltages- indicating that the particular effective elements possess some degree of non-linearity in their response behavior. This behavior is commensurate to the general expectations of the architecture of this device which is essentially constructed as an electrical channel constructed from low-density semi-conductor/semi-metal with a capacitive contact at each end of the channel.

Figure (1C) shows the shift in electrical impedance response that results from exposure of the architecture to water vapor. It may be seen that the response retains the characteristic qualitative single arc of values between approximately 100 Hz and 100 kHz. However, the quantitative values of the impedance are significantly altered and the qualitative characteristics of the arc have shifted somewhat. In particular, the magnitude of both the real and imaginary components of the impedance are substantially reduced for all frequency test values. Additionally, most of the response values for the impedance are more tightly clustered across different applied test voltage values from 0.01V–1V whereas the values obtained at a test voltage of 2V which provides a significantly differentiated response curve.

It is worth recognizing that the VANTA architecture is inherently very low density and the carbon nanotubes constitute a volume fraction typically below 15% and commonly below 1% [19] [20] of the physical space in the spatial region which the structure occupies. As such, applied electrical fields do not terminate at the ‘surface’ of the VANTA as is the case for traditional metals but penetrates for tens of microns into the array [21] which is similar to the Debye length for undoped silicon.

To visualize the impact of the analyte on the system, Nyquist plots have been constructed that shows the shift in device response from a baseline impedance value curve in which the device was purged with N₂ that was taken immediately prior to the analyte test. As such figure (1D) represents the Nyquist plot that results from the figure (1C) after subtracting the data of figure (1B). Thus these figures illustrate the difference of the impedance signal of the device as a result of its exposure to an analyte. It should be noted that this procedure of subtracting the non-exposed baseline data from the device electrical behavior in the presence of chemical analyte simply provides visualization of the difference in measured electrical parameters of the device resulting from chemical exposure. This baseline subtraction is not intended, of itself, to provide direct data regarding the operation of the electrical circuit per se. Further raw data figures are provided in the supplementary information.

Upon exposure to various analytes, the sensor shows both a strong shift in electrical properties in response to all four chemical analytes tested as well as significant differentiating features for each chemical species as shown in figures (1D), (1E), (1F) and (1G).

Water vapor acts to simultaneously reduce the magnitude of the real and imaginary components of the electrical impedance of the device for almost all tested parameter values as shown in figure (1D) while still retaining the basic qualitative characteristics of the circuit behavior. The qualitative shifts in the Nyquist plot suggest that in both real- and imaginary-valued components of the impedance are altered by the presence of water vapor.

In contrast, exposure to organic vapors- ethanol (EtOH), ethyl acetate (EtOAc) and toluene- all led to larger average values for the real component of the impedance as well as larger magnitude negative values for the imaginary impedance component. This again suggests that resistance has been reduced and capacitance has been increased for the VANTA in response to these species. However, the details of the response are different for each species.
Specifically, EtOH, shown in figure (1E), produces a device response wherein the semi-circular arc of the difference signal is roughly maintained and wherein the apparent resistance and capacitance are modified by a similar factor.

Similarly, toluene, shown in figure (1F), the device produces a response wherein the semi-circular arc of the difference signal is roughly maintained and wherein the apparent resistance and capacitance are modified by a similar factor though the details of the response are different for toluene as compared to ethanol.

For EtOAc, shown in figure (1G), the device also produces a response possessing mostly larger average values for the real component of the impedance as well as larger magnitude negative values for the imaginary impedance component. However, for EtOAc, a clear inflection point is seen in the differential curves which is most pronounced for applied test voltage of 0.1V but is seen for all voltages though with decreasing strength for voltages above 0.1V. This inflection point behavior is unique to ethyl acetate out of the analytes tested here.

Conclusions

These data strongly suggest that both the detection and differentiation of chemical environments can be achieved through the use of this architecture as paired with detection based on impedance spectroscopic read-out. Although, clearly significantly more work will be required to fully characterize and understand the nature of the signal arising from the presence of various chemical species.

Limitations

All data shown above was obtained from a single VANTA device. Data has been obtained from other VANTA devices and shows similar qualitative features but the different quantitative response. This is not unexpected as VANTA growth processes are often highly idiosyncratic to the particularities of their growth conditions. Use as a functional device architecture would require better control over VANTA synthesis or a method to calibrate each sensor individually.

In the above, significant drift in the baseline response was observed from run to run over the period of time that these data were collected though the device was relatively stable over short time periods when multiple baseline data sets were collected in succession. Thus all data above is from individual baseline-test cycle sets, follow-up measurements show qualitatively similar features but evident drift. It is considered that methods to stabilize the aging and drift would also be necessary for the practical implementation of this device architecture for sensor devices.

Alternative Explanations

Conjectures

It is conjectured that the polymer adhesive used to transfer and secure the VANTA onto the electrode may significantly contribute to the aging and drift behavior observed for these devices. We anticipate that transfer using non-polymeric materials [22] may be useful to achieve greater stabilization of the VANTA architecture and read-out signal.

Additional Information

Methods

Multi-walled vertically aligned carbon nanotube arrays were obtained from NanoLab and were grown using methods common in the literature. Specifically, the VANTA was
grown from a catalyst of 1 nm Fe over 10 nm Al₂O₃ deposited by DC magnetron sputtering in 3 mTorr Ar. The VANTA was grown at 700°C with 1 atm pressure from a mixture of 100 sccm C₂H₄, 200 sccm H₂, and 500 sccm Ar. Previous characterization of VANTA produced under these conditions have been characterized as typically having a nanotube diameter of around 10 nm and commonly around 3–4 walls with an overall D/G ratio of around 1.5:1. (Further tests- not shown here- have shown responsiveness for VANTA of various nanotube types and structure qualities.)

These arrays were formed as circular pads of 0.5 cm in diameter and approximately 400 microns in height. These arrays were transferred to the surface of a gold electrode supported on a PCB by means of double-sided scotch tape to provide a capacitive electrical connection at the bottom of the VANTA array while a copper gasket ring from a VCR fitting insulated in Kapton tape was allowed to rest on the top of the VANTA array to provide a second capacitive connection while still allowing significant gas-flow through the electrode to reach the VANTA array. This construction creates a device where a vertically aligned nanotube array forms a conductive channel sandwiched between two electrodes at the top and bottom of the array as illustrated in figure (1A). This device was placed into a Teflon chamber with a diameter of 1 cm and a height of 0.75 cm which was sealed to the substrate around the VANTA by an O-ring.

Tests were performed by first equilibrating the array under a flowing stream of dry UHP nitrogen (15 sccm for 20 min) and then the electrical impedance of the device was measured as a baseline and then was subjected to a stream of chemical analyte vapor produced by bubbling dry UHP nitrogen through a vial containing analyte liquid (15 sccm for 10 min) and the electrical impedance of the device was again measured. Water, ethanol, ethyl acetate, and toluene were used as analyte vapors. All tests were therefore taken under an equivalent flow rate of gas after reaching equilibration to the gas stream composition. Impedance spectra were measured using a Tegam 3550 LCR Meter. Impedance measurements were taken over a range of 50 frequencies between 100 Hz – 1 MHz with a log distribution of applied voltages of 0.01V, 0.05V, 0.1V, 0.5V, 1V, 2V. A characteristic baseline impedance spectrum result is illustrated in figure (1B). Impedance spectrum alterations were calculated by subtracting the impedance spectrum of the device during exposure to chemical analyte from the baseline spectrum of the device taken immediately prior to a flow of dry nitrogen.

All test chemicals were supplied by Sigma Aldrich. UHP nitrogen was supplied by Air-Gas.

**Funding Statement**

This work was supported by NanoLab Inc. and ABB Inc.

**Acknowledgements**

Vertically aligned carbon nanotube arrays, intellectual property rights and discussion were provided by David Carnahan at NanoLab Inc.

**Ethics Statement**

Not Applicable.