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Electrochemical Gas Sensor Integrated with Vanadium Monoxide Nanowires for Monitoring Low Concentrations of Ammonia Emission

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An electrochemical sensor for the detection of extremely low concentration of ammonia (1 part per billion, ppb) was fabricated by integrating vanadium monoxide (VOx; x = 0.8–1.2) nanowires on the platinum electrodes. The nanowire-based sensor responds at room temperature non-linearly to a staircase sequence of ammonia from 1 ppb to 100 ppb. The rise and fall time of the nanowire sensor was found to be 10 s and 9 s, respectively. While the immobilization of VO nanowires increased the electrochemical surface area, the defect rich and ionic nature of the VO surface (\(V^{2+}\)O\(^{-}\)) facilitated the chemical interaction and adsorption of polar ammonia molecules as evident in the room temperature response of the VO@Pt amperometric electrochemical sensor. The availability of metal centered d-electrons and the semiconductor nature of vanadium monoxide lowered the interfacial resistance of the nanowire-modified sensor enabling the lower detection limit of ammonia. The sensor seems to respond to CH\(_4\), H\(_2\)S and C\(_3\)H\(_6\) as well although the NH\(_3\) response is nearly six-fold compared to these common interfering compounds. The results pave the way for a low-cost alternative paper-based sensor to monitor ammonia emissions primarily from confined animal feeding operations (CAFOs).

Ammonia gas, at elevated concentrations, is a hazardous pollutant leading to headaches and burning of sensitive tissues.\(^1\) Ammonia can form ammonium nitrate and ammonium sulfate particulate matter, which are carcinogenic.\(^2\) Further, ammonia emissions from confined animal feeding operations (CAFOs) induce toxicity to sensitive ecosystems, eutrophication in surface waters, haze, and environmental acidification.\(^3\) Given the significant societal impact of ammonia emissions, originating from CAFO operations, low cost and efficient sensors are required to address the lack of emission inventories for ammonia since it is not a regulated pollutant in the agricultural sector. The undesired health effects and hospitalizations from ammonia exposures has been reported around a 5 to 10-mile radius\(^4\) from the CAFO source (dairy farm, agricultural farm, or feedlot operation).

To confirm the presence of ammonia and its concentration, hundreds of sensors are required within the 5 to 10-mile radius. Currently available commercial ammonia sensors are not the optimal solution for such widespread deployment due to high cost and maintenance issues. Various field studies to monitor ammonia concentration have reported 5 ppb up to 20 ppm of gas phase NH\(_3\) depending on the size of the dairy/barn/livestock.\(^5,6\) Hence, the desired sensor needs to be low-cost for mass applications and sensitive enough to efficiently detect 1 ppb of ammonia for initiating remediation measures.

Based on field measurements, experts recommend a 1 ppb detection limit for low-cost sensors. Sensors are designed considering specific application. Ammonia sensors can be fabricated on controlled surface with same material combinations and standard techniques. The need for fabrication on a paper substrate is application driven. Monitoring ammonia emissions surrounding CAFOs require mass deployment and needs to user-friendly. The paper substrate is flexible and lends itself to simple integration with flexible potentiostats. They are single use devices. Citizens can wear an arm band containing the device and have an ammonia read-out. With controlled surface, such a feature might be challenging. The motivation for the paper substrate does not solely rely on cost as it is too early to claim cost advantage based on laboratory research. However, the advent of flexible electronics and non-platinum alternatives make flexible substrate a low-cost option for mass deployment.

In this context, direct sampling paper-based sensor implementation is a potentially disruptive technology for fabricating simple, low-cost, portable and disposable analytical devices for many application areas including clinical diagnosis, food quality control, and water pollution.\(^7,9\) Electrochemical modality is ideal to implement paper-based sensors because (a) electrodes can be miniaturized and easily fabricated onto paper, (b) electrochemistry does not require complicated equipment, (c) portable potentiostats are available for on-site measurements, and (d) a wide range of electrochemical sensors are already in commercial space such as the oxygen sensors in vehicles and glucose sensors to monitor diabetes. Paper-based gas sensors operating via an electrochemical modality offers synergistic advantages such as high sensitivity, selectivity, minimal electronic circuitry, low manufacturing costs, and lower detection limits. Table I shows a review of literature on room temperature ammonia sensors implemented on various low-cost substrates in the last two years.\(^10–19\)

The concept of electrochemical ammonia sensor printed on a paper substrate was demonstrated in a previous study by Sekhar et al.\(^19\) in which the electrochemical gas sensor was constructed using platinum electrodes and ionic liquid electrolyte. The amperometric staircase response showed discernible signal differentiation between each concentration of NH\(_3\) (5–25 ppm). Though promising, this potentially low-cost sensor falls short on the detection limit by three orders of magnitude for monitoring NH\(_3\) emission from CAFOs. For reference, Table II shows current ammonia sensing requirements compiled from various literature reports on ammonia pollution monitoring.\(^17,18\) To improve the detection limit, the modification of electrodes with nanomaterials was envisioned in this investigation. Judicious modification of electrodes and electrolyte with nanomaterials is anticipated to result in increased surface area, faster mass transport and improved signal-to-noise ratio. Further, nanoeengineered electrodes ensures smaller RC constants enabling electroanalysis in highly resistive electrolytes. In addition, they potentially result in a small “iR” drop due to extremely small currents.\(^19\)

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| Author (Year)   | Sensing Technique | Electrode/Electrolyte/Active Material                                      | Ammonia Detection Limit and Response time | Interference Rejection               |
|----------------|-------------------|---------------------------------------------------------------------------|-------------------------------------------|--------------------------------------|
| Maity et al. (2018) | Color Change       | Deposition on pervoskite halide on paper                                 | 10–500 ppm 10 s                          | CH₄, CO₂, and N₂O                   |
| Kumar et al. (2018) | Resistance Change  | Polyaniline functionalized multiwall carbon nanotubes                     | 20–100 ppm 9 s                           | Not reported                         |
| Li et al. (2018)    | Resistance Change  | Thermal evaporation of CuBr on a polyimide substrate                     | 5 ppm                                    | Not reported                         |
| Duan et al. (2019)  | Resistance Change  | Conducting polymer nanowire on a PET substrate                           | 100 ppb, 300 s                           | Ethanol, IPA, Xylene                 |
| Patil et al. (2019) | Resistance Change  | (PAni-WO₃) hybrid nanocomposite                                          | 1 ppm, 40 s                              | Not Reported                         |
| Singh et al. (2019) | Resistance Change  | a solvent-free frictional deposition of polymer on paper                  | 200 ppb, 700 s                           | CO₂, CO, Acetone, Ethanol           |
Among the different nanomaterials, nanoscale oxide(s) of vanadium has shown promise in sensing ammonia due to (a) their increased conductance upon exposure to reduced gases such as NH₃ leading to reduced interfacial resistance and (b) promotion of ammonia oxidation on platinum.

In this article, an electrochemical gas sensor for detecting low concentrations (up to 1 ppb) of ammonia is presented. The sensor consisted of vanadium monoxide-modified Pt working electrode with Pt counter electrode, Pt reference electrode and a room temperature ionic liquid as the electrolyte.

**Experimental**

**Synthesis of VO nanowires and characterization.**—One-dimensional vanadium monoxide (VO) nanowires were fabricated according to the solvothermal method by reported Mathur et al. The reaction solution was prepared by dissolving 1.52 g (0.0023 mol) of an air-stable vanadium(III) heteroarylaylenolate (3,3,3-trifluoro-1-(4,5-dimethyloxazol-2-yl)propen-2-ol, [V(DmoxCHF₂)]₃) in 25 ml toluene and 5 ml (0.0015 mol) oleylamine (surfactant) and continuous stirred for 1 h. The orange reaction solution was then transferred to a 60 ml Teflon-tube positioned in a stainless-steel autoclave and heated at 230 °C for 12 h. A black precipitate was obtained after cooling down to room temperature. The powder was washed three times by centrifugation at 11,000 rpm in ethanol. The collected pellet was dried in a desiccator and then calcined under a nitrogen atmosphere for 6 h at 500 °C with a heating rate of 10 °C h⁻¹. Figure 1a shows the Transmission Electron Microscope (TEM) image of the VO nanowires. The numerical density of the nanowires on Pt surface was estimated to be 3 × 10¹² wires m⁻² by counting the wires in five 5 × 5 μm² and averaging them. The average diameter and length of the nanowire was found from a series of TEM images. The average diameter of the nanowires was found to be 210 +/- 31 nm and the average length was found to be 520 μm +/- 17 μm. Powder X-ray diffractogram (XRD, Fig. 1b) revealed the formation of well-defined crystalline phase corresponding to vanadium monoxide (VO) (JCPDS 77–2173).

**Inkjet printing of sensor.**—The printing system used in this study is the Dimatix 2831 Materials Printer from Fujifilm.

### Table II. Summary of current ammonia sensing requirements for widespread measurements.

| Ammonia Sensor Attributes | Current Requirement |
|---------------------------|---------------------|
| Detection Limit           | 1 ppb               |
| Selectivity               | Insensitive to H₂S and CH₄ |
| Power                     | 10–100 nW           |
| Lifetime                  | 6 months if replaceable |
| Cost                      | <$20                |

Figure 1. VO nanowire characterization (a) Transmission Electron Microscope (TEM) image of the VO nanowires, and (b) XRD data showing the crystalline nature of the nanowires and formation of vanadium monoxide.
Results and Discussion

Figure 3 shows the amperometric sensor response from the device working with and without immobilized VO nanowires. From this point onward, the sensors will be referred to as the plain sensor and the nanowire sensor. The nanowire sensor showed discernible current response for various concentrations of ammonia ranging as low as 1 ppb up to 100 ppb. The baseline response was 0 A. The rise time and fall time for the NH3 sensor were found to be 10 s and 9 s respectively. The amperometric ammonia response from the plain sensor (Fig. 3, red colored graph) revealed almost negligible sensor response, whereas several-fold improvement was observed in the VO nanowire sensor. The sensor response magnitude is defined as the difference in current generated upon exposure to the test and base gas respectively.

For 100 ppb of NH3, the nanowire sensor response is approximately 68 times higher than that of the plain sensor. The ammonia sensing mechanism and the sensor enhancement due to the addition of VO nanowires is explained in the next paragraph. The sensing mechanism is based on the oxidation of ammonia on Pt electrodes and vanadium oxide surface. NH3 is oxidized at the Pt working electrode according to:

$$4\text{NH}_3 \rightarrow 3\text{NH}_2^+ + \frac{1}{2}\text{N}_2 + 3e^-$$

The direct oxidation of ammonia in RTILs/Pt is an electrochemical process, where three ammonium ions are formed for every four ammonia molecules, in an overall three-electron process. Ammonia is initially oxidized, to produce nitrogen gas and protons, which readily protonate or are solvated by the RTIL. The protonated anion then reacts further with ammonia, to set up equilibrium with ammonium and solvent ions. Typically, the oxidation of NH3 on vanadium oxide surface involves electron transfer from analyte to VOx surface that produces cationic species (NH2+), which can combine on surface with NH3 molecules to form N2H4 that is oxidized by vanadyl units to N2.24

The enhancement of ammonia response from the sensor with electrodes modified with VO nanowires can be understood by evaluating the electrochemical active surface area and inspecting the impedance spectrum from the devices. The electrochemical surface area of the sensors was determined by the analysis of cyclic voltammogram (not shown) in a ferro-ferricyanide redox couple using Koutecky equation.25 The details of the equation and treatment can be found in an earlier study. The average electrochemical surface area of the inkjet printed Pt electrodes and the Pt electrodes modified with VO nanowires were found to be $6.8 \pm 0.7 \text{ m}^2 \text{ g}^{-1}$ and $572 \pm 8.1 \text{ m}^2 \text{ g}^{-1}$ respectively.

Figure 4 shows the impedance spectrum of the devices when exposed to 50 ppb of NH3. In the Nyquist plot obtained from an electrochemical device, the contributions of the bulk electrolyte and the electrode/electrolyte interface are identified by the frequency dispersions. In general, the low frequency region represents the electrode polarization/charge transfer phenomenon while the high frequency component represents the bulk conductivity of the sample. As the ionic conduction in the electrolyte forms a major representation.

Table III. Ink-jet printing parameters.

| Variable                  | Value   |
|---------------------------|---------|
| Drop Volume               | 10 pL   |
| Nozzle Diameter           | 21 μm   |
| Drop Spacing              | 15 μm   |
| Single Dot Diameter       | 30 μm   |
| Dots per inch             | 1130    |
| Number of printed layers  | 2       |
of the high frequency portion of the Nyquist plot, in further sections, the bulk conductivity of the sample will be approximated to the ionic conductivity of the electrolyte. A significant variation was seen in the low frequency region of the impedance spectrum between the two devices suggesting a difference in magnitude of the interfacial (Electrode/Electrolyte) resistance upon exposure to NH₃.

A quick fitting of the impedance curves indicated the interfacial resistance (R₀) values of 221.2 kΩ and 174.4 kΩ for the plain sensor and the nanowires sample, respectively. The reduced interfacial resistance and increased electrochemical surface area was attributed to the enhancement of sensor response in the nanowire sensor. A comprehensive understanding of the catalytic oxidation of ammonia on vanadium oxide surface is presented in an earlier study.²⁴

Figure 5 shows the current response of the sensors as a function of the ammonia concentration. The X-axis represents the ammonia concentration and the Y-axis shows the logarithmic of the current sensor response. A linear fit was used to model the ammonia response from the nanowire sensor. Upon curve fitting, it was found that the model fitted the data points with an R² value of 0.92. The equation of the fit was found to be:

\[ y = 0.00403 + 0.000155x \]

where, “y” represents the logarithm of the current value and “x” represents ammonia concentration. The response of the nanowire sensor to varying ammonia concentration was complex (non-linear) and directly dependent on several factors, including heterogeneous catalysis, and the kinetics of electron transfer at the dense electrode/nanowire interface. It was important to study the cross-sensitivity of the nanowire sensor to CH₄, H₂S and C₃H₆ since these compounds are also found in the emissions from CAFOs. Figure 6 shows the interference test resulting from the nanowire sensor. All the analytes were maintained at 50 ppb and tested independently.

The sensor exhibited a dominant response to ammonia. Further, the sensor seemed to respond to CH₄, H₂S and C₃H₆, although the NH₃ response is nearly six-fold compared to those of the commonly interfering compounds.

Future investigations are necessary to validate the ammonia sensor closer to the field tests. The variability in the sensor response (indicated by error bars) needs further exploration and detailed analysis on the paper architecture. Such a study is needed to understand the effect of tuning the layering for repeatable fabrication as each paper type is different and materials will interact differently depending on the wettability, porosity, etc. In addition, the authors envision the following tasks as future activities: (a) perform interference testing in a mixture amidst high humidity levels; (b) pursue long-term testing of the sensor to identify any aging; (c) introduce hydrocarbon and H₂S filter; and (d) implement antennas on the paper substrate co-located with the sensor for wireless transmission of data.

Conclusions

In this article, a room temperature electrochemical gas sensor was reported to detect extremely low concentration of ammonia...
(1 ppb) primarily for CAFO applications. The low detection level was possible due to the modification of the platinum electrode of the amperometric sensors with VO nanowires. The rise and fall time of the nanowire sensor was found to be 10 s and 9 s respectively. The addition of VO nanowires resulted in a remarkable 84-fold increase in the electrochemical surface area of the device and 21% reduction in interfacial resistance, when compared to the plain sensor. For 100 ppb of NH₃, the nanowire sensor response was found to be approximately 68 times higher than that of the plain sensor. The nanowire sensor seems to have a dominant ammonia response compared to CH₄, H₂S and C₃H₆.

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