New organic semiconductor based sensors for nitro compounds

Robert Blue, Zuzana Vobecká, Peter Skabara, Deepak Uttamchandani
To fabricate and experimentally evaluate micro sensors designed for detecting explosives (through vapours)

- Synthesise nitro-sensitive receptor monomers
- Controllably grow the polymers on the micro fabricated sensor using electropolymerisation
- Electrical properties of polymer changes reversibly in presence of target compound – detected by the sensor
Explosives Detection

- **Requirements:**
  - miniaturized (portable/wearable) sensors
  - low-cost
  - fast response times
  - wireless, networked

- **Applications**
  - transport hubs
  - sports arenas
  - shopping malls,...
## Classification of Explosives

<table>
<thead>
<tr>
<th>Compound class</th>
<th>Example</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aliphatic nitro (C-NO₂)</td>
<td>Nitromethane</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydrazine nitrate</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2,3-dimethyl-2,3-dinitrobutane</td>
<td>DMNB</td>
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<td>Aromatic nitro (C-NO₂)</td>
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<td>NT</td>
</tr>
<tr>
<td></td>
<td>2,4,6-trinitrotoluene</td>
<td>TNT</td>
</tr>
<tr>
<td></td>
<td>2,4-dinitrotoluene</td>
<td>DNT</td>
</tr>
<tr>
<td></td>
<td>2,4,6-trinitrophenol (Picric acid)</td>
<td>TNP</td>
</tr>
<tr>
<td>Nitrate ester (C-O-NO₂)</td>
<td>Nitroglycerine</td>
<td>NG</td>
</tr>
<tr>
<td></td>
<td>Ethylene glycol dinitrate</td>
<td>EGDN</td>
</tr>
<tr>
<td></td>
<td>Pentaerythritol tetranitrate</td>
<td>PETN</td>
</tr>
<tr>
<td></td>
<td>Nitrocellulose</td>
<td></td>
</tr>
<tr>
<td>Nitramines (C-N-NO₂)</td>
<td>Trinitro-triazacyclohexene</td>
<td>RDX</td>
</tr>
<tr>
<td></td>
<td>Tetranitro-tetrazacyclooctane</td>
<td></td>
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**Laboratory Testing:**

- Nitrotoluene
- Nitrobenzene
- Nitropropane
Explosives Detection

Methods applied
- Spectroscopic methods: ion-mobility spectroscopy (IMS), MS, GC
- Metal detectors
- X-ray dispersion, Terahertz imaging
Explosives Detection

Methods applied
- Spectroscopic methods: ion-mobility spectroscopy (IMS), MS, GC
- Metal detectors
- X-ray dispersion, Terahertz imaging
- Trained canine teams
Miniaturising Explosive Sensors – Current Research

Mass sensors
Miniaturising Explosive Sensors – Current Research

Mass sensors

Optical sensors

trinitrophenol (TNP)
Miniaturising Explosive Sensors – Current Research

Mass sensors

Optical sensors

Receptor-based sensors

trinitrophenol (TNP)
Miniaturising Explosive Sensors – Capacitance Sensors

For $\varepsilon_0$, $A$, $d$ constant:

$$\text{Capacitance} = \frac{\varepsilon_0 \varepsilon_r A}{d}$$

Capacitance varies with polymer relative permittivity $\varepsilon_r$. 
Seacoast Science Inc. (USA)
(founded 2003)

- “Off-The-Shelf” polymer deposition by inkjet printing
- Spot diameter 30 to 100 microns
- Polymers have sensitivity to most atmospheric vapours, often of similar magnitude
Seacoast use an array of sensors with different polymers combined with pattern recognition algorithms.
# Seacoast LDC Data

## Table 1. Demonstrated* detection capabilities of Seacoast Science’s capacitive sensor

<table>
<thead>
<tr>
<th>Class</th>
<th>Chemical</th>
<th>LDC* (ppm)</th>
<th>Chemical</th>
<th>LDC* (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CWA Simulants</td>
<td>Chloroethylether</td>
<td>1</td>
<td>Methyl Salicylate</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>Diisopropyl-methylphosphonate</td>
<td>0.1</td>
<td>Dimethyl methylphosphonate</td>
<td>0.1</td>
</tr>
<tr>
<td>Organic</td>
<td>Acetone</td>
<td>11</td>
<td>Hexadecane</td>
<td>0.097</td>
</tr>
<tr>
<td>Compounds</td>
<td>Acetonitrile</td>
<td>25</td>
<td>Isopropyl Alcohol</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>Benzene</td>
<td>13</td>
<td>Methyl Alcohol</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>Bromobenzene</td>
<td>7</td>
<td>Octane</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>n-Dodecane</td>
<td>46</td>
<td>Tetrahydrofuran</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>Ethyl acetate</td>
<td>17</td>
<td>Toluene</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>Allyl Alcohol</td>
<td>43</td>
<td>Phenol</td>
<td>1.85</td>
</tr>
<tr>
<td></td>
<td>Ethyl alcohol</td>
<td>63</td>
<td>Acetophenone</td>
<td>1.8</td>
</tr>
<tr>
<td>Nitro-</td>
<td>Nitrobenzene</td>
<td>1.3</td>
<td>Nitropropane</td>
<td>133</td>
</tr>
<tr>
<td>compounds</td>
<td>Nitrotoluene</td>
<td>2</td>
<td>2,6-Dinitrotoluene</td>
<td>0.004</td>
</tr>
</tbody>
</table>

*Lowest Detected Concentrations (LDC) were achieved without analyte pre-concentration in a laboratory controlled flow system in dry or 50% RH conditions.

From Seacoast Technical white paper
Electrochemical Deposition

Advantages:

- Fast, high-yielding and *in situ* polymer synthesis whilst using minimal amounts of monomer
- Eliminates multiple steps in the sensor fabrication process
- Clean synthesis and elimination of the need for multiple reagents and catalysts
- Depending on the monomer structure, the polymerisation can be performed in a wide range of solvents (or even in water)
- Specify deposition location and film thickness to sub-micron range
Interdigitated Capacitors

Capacitance = \( \frac{\varepsilon_0 \varepsilon_r A}{d} \)

Electrode gap sizes used: 1 to 20 microns
Polymer Electrochemically Grown from Monomer

Uncoated Electrodes

copolymer growth localised to electrodes
Sensor Test Chamber

- Agilent 4294A 4980A
- Paraffin oil
- Temperature and Humidity
- Water Bath
- Volatile Organic Chemical Sample
Results: nitro-group sensor vs “off-the-shelf” polymer
## Cross-sensitivity to common atmospheric vapours

<table>
<thead>
<tr>
<th>Chemical Vapour Tested (Saturated Vapour)</th>
<th>Capacitance before exposure to vapour $C_1$ (picoFarads)</th>
<th>Capacitance after exposure to vapour $C_2$ (picoFarads)</th>
<th>Relative Change $(C_2 - C_1)/ C_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitropropane</td>
<td>7.24</td>
<td>529.80</td>
<td>72.22</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>7.53</td>
<td>315.63</td>
<td>40.92</td>
</tr>
<tr>
<td>TetraHydroFuran</td>
<td>6.77</td>
<td>7.25</td>
<td>0.072</td>
</tr>
<tr>
<td>Methanol</td>
<td>7.10</td>
<td>7.54</td>
<td>0.062</td>
</tr>
<tr>
<td>Toluene</td>
<td>7.13</td>
<td>7.33</td>
<td>0.029</td>
</tr>
<tr>
<td>Octane</td>
<td>7.03</td>
<td>7.19</td>
<td>0.023</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>7.00</td>
<td>7.04</td>
<td>0.0047</td>
</tr>
</tbody>
</table>
Expt Setup: dynamic flow

- Nitrogen
- Dessicator
- Paraffin oil
- P1, P2, F1, F2
- Digital Pressure Meter
- Temperature & Humidity
- Agilent 4294A 4980A mixer
- Test Chamber
- VOC Sample
- Paraffin oil

Test Chamber includes exhaust connections for Nitrogen.
Lower Concentrations

(Assuming saturated vapour flow)
Nitrobenzene detected over sub-100ppm range
Future Plans

Conjugated microporous polymers

- Increased surface area – higher sensitivity and faster response
- Incorporating other molecules or ions inside the pores

- Linear polymer

- Crosslinked polymer
Future Plans: 3D MEMS
Conclusions

- The synthesis of custom (polymer) materials having specific electronic properties rendering them suitable as sensors for target (nitro) molecules

- Viability of localised electrochemical polymerisation as a manufacturing process which uses low-capital-cost equipment

- Creation of sensors which show a reversible response to nitro-bearing compounds, and more than 100 times greater in magnitude compared to other organic vapours
Acknowledgments:

IeMRC: Innovative electronics Manufacturing Research Centre

Thank you for your attention!