Advances in Optical Sensing of Explosive Vapours

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Abstract: Optical techniques for the detection of explosives are receiving increasing interest due to potentially fast-responding, highly-sensitive systems. Conjugated polymers are suitable probe materials for this application since their fluorescence is quenched by electronegative materials including explosives. This can be used to make a sensor for explosive vapour, which can then give chemical information to help identify explosive devices, and complements other approaches such as metal detectors and ground penetrating radar. Whilst the principle has been known for some time, its practical implementation requires considerable development of instrumentation and materials, including preconcentration materials. This paper reports our current efforts to address these challenges, with particular emphasis on humanitarian demining and looking towards application in Improvised Explosive Device (IED) detection.

1 INTRODUCTION

Of the many challenges in explosives detection, detecting trace amounts of vapour from buried or otherwise hidden explosives is one that could lead to huge advances in the field. Conjugated polymers are well-suited to explosive vapour detection since they exhibit bright photoluminescence, are solution-processed, and readily undergo photoluminescence quenching by electron-deficient materials like nitroaromatics when exposed to vapours (Rose et al., 2005, Thomas et al., 2007).

The advantage of using photoluminescence for sensing the chemical signature of explosives is that this quenching effect can be monitored by a photodiode and integrated into user-friendly, inexpensive, portable instrumentation. Common explosive/landmine detecting technologies have disadvantages that can potentially be mitigated by chemical sensing; for instance, metal detectors can miss plastic mines, sniffer dogs can be temperamental, and other methods such as Ion Mass Spectrometry do not lend themselves to portability. The use of photoluminescent conjugated polymer films can be adapted for use in varying architectures according to the specific requirement whether this is vapour detection, aqueous environments, forensic sampling, or moving towards methods for specificity and selectivity.

This paper gives a brief overview of current ongoing efforts on the optical detection of explosive vapours being conducted in our laboratories. By developing a suite of discrete methods that can potentially be integrated, there is potential impact to humanitarian demining and Improvised Explosive Device (IED) detection.

2 INSTRUMENTATION

One of the main advantages of using photoluminescent materials is the ability to monitor emission intensity as it is quenched using photodiode or CMOS detectors. This then can lead to portable, modular, inexpensive and user-friendly systems for detection of explosive vapours in the field.

We have successfully developed instrumentation to sense explosive vapours (Gillanders, 2017), using photoluminescence quenching from a conjugated polymer excited by an LED. Photoluminescence was collected by a Hamamatsu photodiode and data processed by an off-the-shelf microprocessor (Arduino Uno). This system successfully detected buried explosive

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vapours with a Limit of Detection (LoD) of 30 ppb for 2,4-Dinitrotoluene (2,4-DNT), with promising properties with respect to reproducibility, low-cost, user-friendliness, and sensitivity.

We have also developed an optical system based on a CMOS camera and Raspberry Pi platform (Gillanders et al., 2016). The CMOS camera-based system provides a route to array sensing, since the camera is sensitive enough to monitor photoluminescence quenching in real-time from multiple polymer sensor films.

These open-source, inexpensive microprocessors offer benefits to instrumentation development, including rapid-prototyping, low-cost, and portability. Close collaboration and feedback from end-users helps direct the system development for realistic field deployment scenarios.

3 MATERIALS & METHODS

3.1 Conjugated Polymer Properties

A number of conjugated polymers are commercially-available, including Super Yellow from Merck, and F8BT and Polyfluorene (PFO) from American Dye Source (Wang et al., 2012, Bolse et al., 2017). While all three have demonstrated good sensitivity to nitroaromatics, each polymer has a distinctive response to various explosive vapours. For instance, Super Yellow, illustrated in Figure 1, exhibits strong sensitivity to 2,4-DNT, a common by-product of TNT and constituent found in many landmines. F8BT, on the other hand, shows a higher quenching response to TNT. This difference in response from each polymer can enable a multi-sensor approach to "fingerprint" a specific explosive vapour, for instance by using the CMOS camera-based system described above to monitor multiple sensing polymers simultaneously. Thus, by developing a library of vapour-polymer responses, identification of the nitroaromatic vapour could be achieved helping to reduce false positives in the field, which might arise from distractants such as pesticides.

Films based on these materials have some drawbacks including lumophore degradation caused mainly by photo-oxidation when excited under ambient conditions. However, this may be mitigated in part by monitoring gradual photoluminescent degradation of a pristine film, in comparison with the faster exponential decay of an analyte quenching event (Gillanders, 2017).

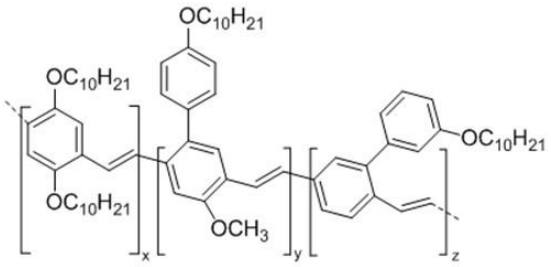

Figure 1: Structure of Merck Super Yellow.

3.2 Rest Sampling

Remote Explosive Scent Tracing (REST) is a common method for technical surveys of an area to determine the presence of explosive materials, and is used after clearance activities for Quality Assurance (QA) (Lugo et al., 2017). Typical practice involves sample collection of air and dust across a suspected site into a polyethylene net filter prior to sending the sample to a dedicated centre to be analysed with sniffer dogs. This method is time-consuming and may be subject to inconsistencies from the canine behaviour. By adapting the optical system for use on-site, the timeline of sampling could potentially be decreased from weeks to hours.

We adapted a method used previously for Surface Acoustic Wave devices (Houser et al., 2001, Voiculescu et al., 2006) and separation science (Egorov et al., 2006, Grate et al., 2007) where a polymeric material sorbs vapours, which can then be thermally desorbed by heating to around 60°C. This technique, known as preconcentration, enables a higher mass of explosive particles to be collected and delivered to the sensor material.

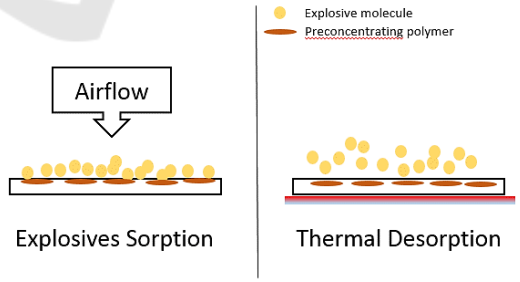

Figure 2: Sorption of explosive materials to a fluoropolymer-spotted paper substrate via air-sampling and subsequent thermal desorption for delivery to sensor.

We used a commercially-available polymer known as Aflas as the preconcentrating polymer. As illustrated in Figure 2, the polymer was spotted on a filter paper substrate then placed in the nozzle of an air pump and air was sampled for 10 minutes at 60

L/min. The filter was transferred to a sealed heating chamber, heated to 60°C, then a valve was opened exposing the atmosphere of the preconcentrating chamber to the Super Yellow sensing film, and the photoluminescence intensity recorded.

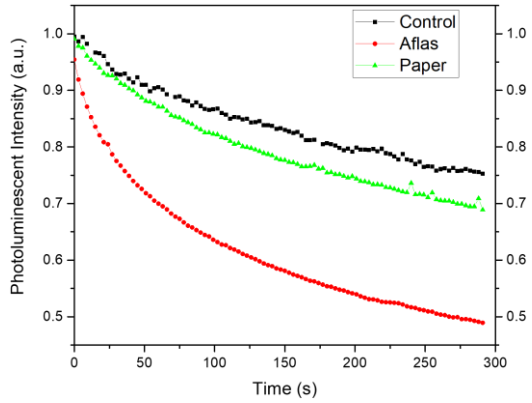

Figure 3: Benchtop tests with an unexposed Aflas-spotted filter paper (Control, black line), uncoated filter paper (Paper, green line), and an Aflas-spotted filter paper (red line) exposed to DNT vapour.

The quenching response of Super Yellow to preconcentrated 2,4-DNT vapour is shown in Figure 3. The Control line, which was a clean Aflas-spotted filter paper, gives a quenching response of around 25%, which can be attributed to thermal degradation. The unspotted filter paper gives a slightly higher quenching response of 30%, which suggests the filter paper can sorb explosives to some degree. The Aflas-spotted substrate gives a quenching response of over 50%, indicating that the material is well-suited as a preconcentrating material. The advantage to this is that the material is inexpensive, solution-processed, and can be prepared in large batches by a variety of coating methods, including spotting, dip-coating, and blade-coating.

3.3 Swabbing

Swabbing is widely-used in security applications or in post-blast forensics (Borusiewicz et al., 2013, Ceco et al., 2014) to sample trace particles of explosives. Swabbing is commonly seen in airports, where hand-luggage is swabbed prior to analysis by Ion Mass Spectrometry.

The preconcentration materials described in Section 3.2 may also be deployed in a swabbing procedure where it could be used to pick up explosive residues on luggage, packages, door handles and other objects. This has particular potential for IED detection where fast positive detection can be crucial in the timeline of a terrorist plot. Initial results indicate this is a promising tool for fast detection of explosive residues on common objects. Work is ongoing to improve instrumentation to allow in-field detection with minimum false positives.

3.4 Explosives in Aqueous Environments

Detection of explosives in aqueous environments is a challenge spanning landmines in humid or waterlogged environments, port security, wastewater monitoring for detection of IED factories, post-detonation forensics, and water quality monitoring in contaminated sites, including munitions factories. However, conjugated polymer films typically are not robust enough for aqueous deployment, especially over long periods of time.

Ormosils have been applied to photoluminescent polymer films as barrier coatings to exclude water from the sensor layer (Gillanders et al., 2018). However, the structure of the material allows the analyte to diffuse through the pores, resulting in a reversible, robust explosives sensor for aqueous environment. Figure 4 shows the typical photoluminescence response of a Super Yellow film coated in an ormosil layer to concentrations of 2,4-DNT from 7.2 μM to 7.2 mM, with a Limit of Detection of 8.24 μM (0.22mg/L).

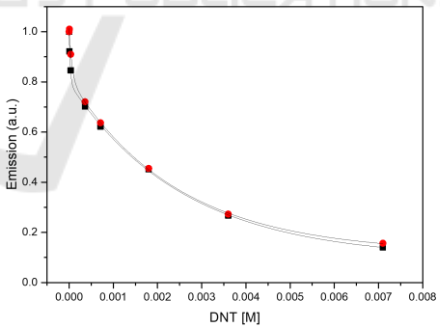

Figure 4: Photoluminescenct quenching response of an ormosil-coated Super Yellow layer to concentrations of 2,4-DNT from 7.2 μM to 7.2 mM.

Preliminary work has been performed on extraction of explosive materials from soil for detection by optical interrogation. This allows for soil samples to be analysed for the presence of explosives, and potentially identified using specificity or selectivity tests. Figure 5 shows extraction of 2,4-DNT from soil. The concentrations spiked into the soil samples were 600 mg/L, with 106 mg/L, 228 mg/L and 260 mg/L recovered. For

comparison, the typical level of TNT found in wastewater of a TNT factory is 156 mg/L (Barreto-Rodrigues et al., 2009). With the sensitivity shown by the ormosil-coated aqueous explosives sensor, these typical levels of nitroaromatic compounds can be detected in the field.

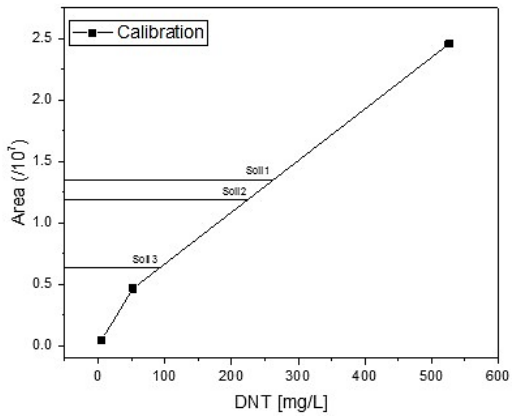

Figure 5: Calibration curve of DNT in Acetonitrile. Three identical vials of 3g soil spiked with 600 mg/L DNT in water were added (absolute mass approx. 2 mg DNT per vial), left overnight, sonicated with MeCN then the solvent extracted and run through a HPLC.

4 CONCLUSIONS & OUTLOOK

The use of light-emitting polymers for nitroaromatic sensing has been described in several different configurations, including vapour sampling, REST sampling, and aqueous detection, to help address the many challenges in explosives detection. While all of the strands in this research are in progress, efforts have been made particularly towards portable optical sensing systems which have been developed and characterised, and further development of sol-gel barrier films for aqueous sensing, and imprinting for specificity are being investigated. Counter-IED applications of these technologies and methods are under increasing focus since global interest in explosives detection is tending towards IED detection in areas including anti-terrorism activities, airport security, and crowd screening. Parallel development of instrumentation with materials and methods for increased specificity and selectivity can lead to reliable in-field detection, which can potentially have a positive impact on humanitarian demining and Counter-IED activities across the world.

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