The development of light-emitting polymer sensors to detect explosives for humanitarian demining

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Abstract — This paper presents an overview of progress towards the development of a compact polymer-based explosives vapour sensor, under development within the TIRAMISU project for the detection of landmines. Materials optimisation of the sensor films is discussed and a novel LED-powered polymer laser sensor is presented.

1. Introduction

A current challenge for the mine action community is how to increase the efficiency of landmine clearance. The TIRAMISU Project aims to address this issue by developing a toolbox of detection and disposal tools that advance and complement the technologies currently in use. In humanitarian de-mining it is necessary to achieve complete removal of explosive ordinance before land is released back to the local community. The processes of close-in detection and disposal of landmines is slow and costly, and so it is important both to identify the correct search area and to minimise the false alarm rate of positive detections.

Close-in detection of buried landmines commonly uses metal detectors. However these can suffer from false positive detections of innocent fragments of metal. Combining metal detectors with ground penetrating radar can help to reduce false detections, but it would still be desirable directly to detect the presence of explosives in the proximity of a possible landmine. An approach which sensitively detects explosive vapours in a technology that could be correlated with a metal detector search would help characterise buried objects as landmines.

One approach to reducing the area required for mine clearance is to make a technical survey using remote explosive scent tracing (REST). The REST technique involves drawing air and dust into a storage filter, to sample for explosives over a survey area. The filter is subsequently presented to animals (dogs or rats) to sniff for traces of explosives[1]. This approach has been successfully implemented with animals by Mechem and others, but there could be advantages in using a sensitive electronic detector that can quantify the explosive residue in the filter, or even identify the constituents.

Within the TIRAMISU project, we are currently developing novel polymer-based sensors for detecting explosive vapours from landmines. These sensors work by detecting a change in the light emission from a semiconducting polymer film.[2] When exposed to very dilute vapours of TNT-like compounds, the explosive molecules adhere to the film and turn off the light emission, due to a molecular interaction between the polymer and sorbed TNT molecules (figure 1). If the plastic film is removed from the vapour, the concentration of explosives molecules in the film decreases and the light emission returns to its original efficiency. In this paper we describe progress towards the development of a compact polymer-based explosives

vapour sensor that could be used for on-field mine detection. We describe the underlying principle of operation, optimization of polymer film properties for fast detection and implementation of a compact prototype sensor using a plastic laser powered by an LED.

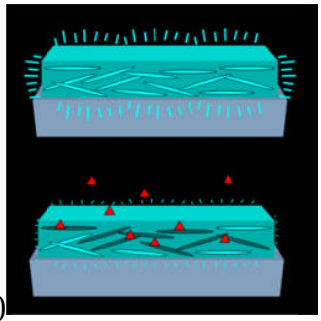
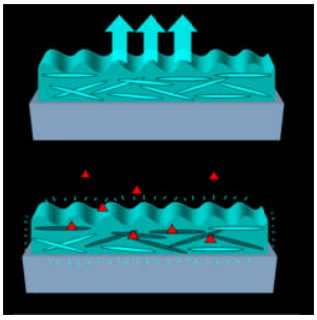
(a)  (b) 

Figure 1. (a) concept of explosive vapour sensing using fluorescent polymer films (a) and polymer lasers (b). (a)Top panel shows blue fluorescence from a film of pollymer molecules (blue rods). Bottom panel shows effect of TNT vapour exposure- when the TNT molecules (red triangles) come into contact with the polymer chains they switch off much of the light emission. (b) Top panel shows a blue laser beam emitted from a corrugated film of. Bottom panel shows effect of TNT vapour exposure, switching off the laser emission, leaving only weak fluorescence.

2. Principle of sensor operation

The underpinning principle of detection is via a change in the light emitted from a luminescent semiconducting polymer film.[2] When a very thin film, typically a few 100 nm in thickness, is illuminated by UV or blue light, it absorbs the light and re-emits it in a longer wavelength range as fluorescence. If the film then comes into contact with explosives vapours such as TNT or a similar nitro-aromatic compound, some molecules of the vapour will adhere to the surface of the film and may penetrate deeper into the polymer. These explosives molecules can then have a dramatic impact on the light emission. For now if the UV light is absorbed in the film near one of the explosives molecules, it is more likely that the photo-excited polymer will transfer an electron to this molecule than emit light. As a result the light-emission from the film rapidly decreases with time (see for example figure 2 for the change in light emission from a polyfluorene film when exposed to vapours of various analytes). If the plastic film is then removed from the vapour, the equilibrium concentration of explosives molecules in the film decreases and the light emission returns to its original efficiency. Fluorescence sensing has previously been studied in laboratory conditions and in the field as the Fido sensor from Flir Systems.

As well as having an effect on fluorescence, the presence of the explosive vapour can also quench laser emission from the polymer films.[3-6] When suitably designed and photopumped with intense pulses of light, the luminescent polymer films can generate short pulses of laser light.[7] Usually this involves a configuration in which the polymer film is deposited on a nanostructured substrate to form a plastic distributed feedback resonator (figure 1(b)). Above a characteristic minimum excitation intensity of a pump laser (the so-called laser threshold), laser action from the polymer film starts, emitting a well-defined beam of light from the surface of the film. The presence of the explosive vapour can increase this laser threshold thereby switching the polymer laser between laser emission and normal fluorescence, and

affect other characteristics of the laser operation. The lasers have potential for higher sensitivity and faster response to the presence of the explosive vapours than fluorescence based sensors.[4-6]

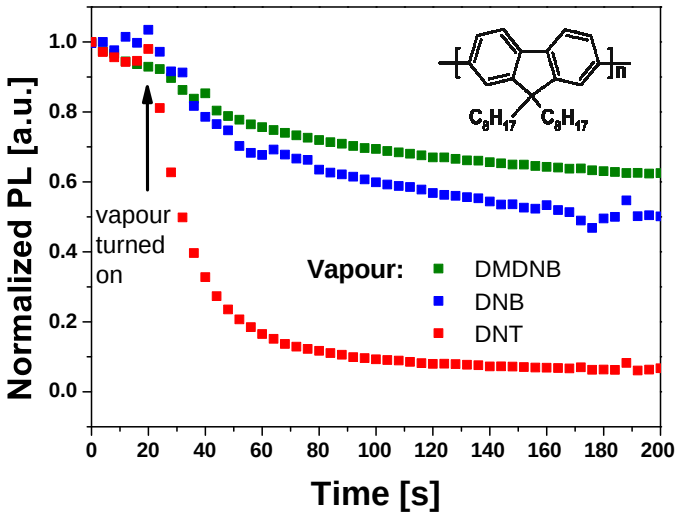


Figure 2. Example response of a polyfluorene sensor to DNT, the simulant DNB and taggant DMDNB. Inset shows molecular structure of polymer.

3. Molecular optimisation of polymer sensor element

The development of the explosive sensor requires optimizing the response to nitro-aromatic vapours (including speed of response, sensitivity, selectivity and ability to reset the sensor). Once the vapours have been sorbed into the polymer film, the change in light emission depends on interactions between the molecules on very short length-scales. To control these, we have studied various aspects of the molecular design, film conformation and preparation processes.

We have been studying how the molecular design of the light-emitting material can offer the best configuration for future sensor applications. This is achieved through vapour sensing tests using families of molecules with systematic changes in the length of the side arms off the polymer backbone. Such studies allow nanometre-length control of the gaps between the molecules in the sensor film, which can potentially affect the sorption of explosive molecules into the film and the efficacy of the sensor quenching mechanism. We find that denser films can improve the speed of response and sensitivity to vapours.

We have also been exploring how to optimise the fabrication of the polymer film. The deposition process for the polymer film can strongly affect the molecular confirmation, and in turn its optical and sorption properties. During this study it was found that the spin coating of films of polyfluorene from different solvents, and at different temperatures, could significantly affect the sensitivity of the sensors. We found that an enhancement of the sensitivity and recovery (sensor reset) process for the sensor can be obtained by controlling the amount of β-phase molecules in a polyfluorene film (the β-phase is a more ordered molecular confirmation of polyfluorene polymer).

4. LED-powered polymer laser sensor

A key step to compact and light-weight versions of a polymer laser based vapour sensor is to achieve very low-threshold laser operation to allow them to be combined with a compact pump source. We developed state-of-the-art polymer lasers that can be integrated with, and powered by, a pulsed LED as shown in figure 9, and showed that the laser could be used to detect ppb levels of nitroaromatic vapours, with scope to detect lower concentrations. Details of this prototype sensor was published in Laser and Photonics Reviews.[8]

The laser was based on the green fluorescent polymer BBEHP-PPV and configured as a surface-emitting distributed feedback laser. This was fabricated by depositing a thin film of the light-emitting polymer on a specially designed nanostructured glass substrate which controls the propagation of light in the film. The laser was mounted in contact with a commercial blue LED, which was driven with a pulsed current source. Above a threshold LED intensity the film emits a green laser beam, which was detected and characterised by a spectrometer and fast photodiode.

We investigated the response and sensitivity of the InGaN LED pumped BBEHP-PPV laser sensor to the presence of dinitrobenzene vapours (a simulant for TNT/DNT with a vapour pressure similar to TNT).[8] We monitored changes in the LED intensity required to initiate laser action and in the output efficiency of the plastic laser. The DNB concentration was varied in the parts-per-billion range using a calibrated vapour source. These studies show that the preferred approach for gaining the lowest limit of detection will be to monitor the change in the laser emission intensity when the sensor is operated in a regime in which the presence of vapours can switch it from laser operation to fluorescence, Figure 9. Experiments to extend these measurements to lower concentrations are underway by combining a commercial Owlstone OVG-4 vapour source with an in-house designed apparatus for vapour dilution.

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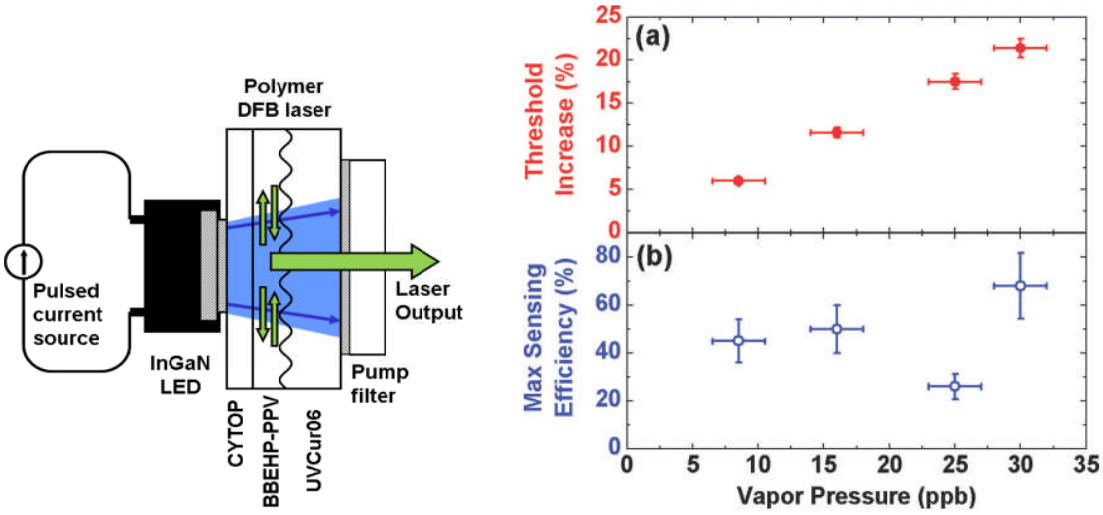

Figure 9. Left: schematic design of the LED-pumped polymer laser sensor. Right: (a) Increase in the laser threshold due to the exposure to the different DNB vapour pressures (b) maximum sensing efficiency of the laser sensor as a function of DNB vapour concentration. Reproduced with permission from reference [8].

5. Modular design of compact sensor system

We are currently developing a compact and portable vapour sensor system suitable for field tests planned in 2014 and 2015. The portable sensor system has a modular design, and several different modes of operation are anticipated for explosives detection:

- *Stand-alone "safe/unsafe" operation*. This base functionality allows the user to operate the platform with the aim of detecting the presence of explosive vapours; when vapour is detected an audio-visual alarm is triggered. This method indicates a threshold quantity detected but does not provide more quantitative information
- *Integrated monitoring*. The sensing system will monitor changes in light emission which should be able to be calibrated to provide vapour concentrations according to the received signal from the microprocessor. In this mode the sensor output is sent via USB to a computer; this can be upgraded to communicate wirelessly at a future stage. It is expected that power can be supplied by the carrier vehicle/robot in the field, but an internal battery can supply power otherwise.
- *Polymer laser explosive detection*. This functionality includes a commercial laser head to pump the polymer film (which is configured as a polymer laser), where the polymer laser emission is subsequently quenched by introduction of explosive vapour into the polymer matrix. For more robust operation in initial trials, a commercial pump laser has been selected for the initial implementation. It is envisaged that this could be replaced in the future by the more compact LED pump module.
- *Photoluminescence explosive detection.* This method is similar to the threshold detection functionality, and offers the potential for a lower weight and power implementation by using a simpler excitation source, but may not provide the same level of sensitivity or response time.
- *REST filter sampling.* The sensor will interface with a REST filter in a sealed container to allow it to measure the equilibriated vapours in the container. In preliminary tests we have found that vapours from explosive particles can readily be detected after 20 minutes settling time (at 20°C) for particle mass/container volume ratios down to ng/ml. With longer settling times and higher temperature, lower limits of detection are anticipated.

6. Conclusions

Within the TIRAMISU project, we are developing compact sensors to detect vapours of explosives from landmines and other unexploded ordinance. We have been optimising the response of detection of polymer films through studies of molecular design, processing and with combinations of different materials. A prototype test using an LED-powered polymer laser sensor has been successfully shown to detect nitroaromatic vapours, and a modular compact sensing system is currently under development. During the next phase of the project, the optimised materials will be tested in the compact sensor system, in laboratory and field

tests during 2014 and 2015. Another aspect of ongoing research involves the improvement of the selectivity of the sensor to discriminate against potential distractions in the field.

7. Acknowedgements

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