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Molecularly Imprinted Optical Fibre Sensor for Detection of Nitroglycerin

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ABSTRACT

In this study, a nitroglycerin (NG) sensor has been developed, utilizing indium tin oxide (ITO) coated optical fibres, molecularly imprinted polymer (MIP) and xerogel technologies. Nitroglycerin detection remains of great importance in the defense and security industry and therefore, steps towards sensitive and specific detection technology are important to be explored. Experimental methods reported focus on the removal of NG from the MIP, evidenced by a change in wavelength shift, (38.62 nm), indicating that NG was fully removed, before exploring the rebinding and subsequent quantification of NG uptake in follow-up analysis. A non-imprinted polymer (NIP) has been developed in parallel and measurements made, to compare the performance and behaviour of the MIP. The chemical sensor scheme developed here shows promise for detecting NG using the technologies discussed, and while most relevant to the defense and security applications, they also have side applicability to different targets for other industries.

Keywords: explosive detection, nitroglycerin (NG), optical fibre sensors (OFS), xerogel, molecularly imprinted polymers (MIPs), chemical sensors, lossy mode resonance (LMR), indium tin oxide sensors (ITO)

1. INTRODUCTION

In the past 45 years, the defense industry, and by proxy, the aviation industry has drastically increased security measures – amongst them improving their explosive detection capabilities, to prevent possible terrorist attacks such as the Lockerbie bombing as well as the Underwear Bomber. As the technologies become more sensitive and therefore limits of detection become lower, those wanting to evade these security measures to perform acts of terrorism, try to find innovative ways to do so, and as a result, there is always an increased need for sensors showing lower levels of detection for molecules of interest, such as nitrogen-containing compounds. As an example, NG is a prominent component in explosives, particularly dynamite, and with a high sensitivity to shock and friction as well as a high detonation velocity. NG is also well-suited to applications in the construction and firearm industries given its powerful explosive capacity, and it is these same characteristics that appeal to those involved in acts of terrorism.

Technologies to support this industry, with an aim to prevent these attacks, and specifically to enhance detection of explosives, have varied throughout the years: however, there has been little research on molecularly imprinted polymers (MIPs) or advantage taken of their compatibility with optical fibres, to create innovative sensors (OFSs) ¹. Optical fibres are well-known for their sensor applications; they provide a platform resistant to external stimuli, and MIPs are well-known taking advantage of their specificity and selectivity features, especially for explosives detection. MIP technology involves imprinting a polymer matrix with a template, i.e., the analyte of interest and after subsequent removal of the template (usually through solvent extraction), the polymer matrix leaves gaps specific to the template, enabling that template to rebind in a given environment if the target molecule is present. However, there is a relatively small number of publications where the two (MIP and OFSs) technologies are combined, for example in illicit drug detection ²⁻⁴ amongst others. The detection of nitroglycerin has been the focus of a number of papers, (often with a focus on its use in the medical field), but there are fewer where molecularly imprinted polymers are used. For example, work has been published on

nitroglycerin in its medical context (as a medication taken for angina) and a controlled-release model in biological fluids with respect to drug delivery⁵. The research in this study, however, concerns the application of nitroglycerin detection, and related technology, to security applications.

This research therefore investigates the development of a molecularly imprinted polymer-optical fibre sensor (MIP-OFS) scheme, where the target analyte is nitroglycerin. Its subsequent removal, as the removal step in MIP creation is the time-limiting factor but also, the most crucial step for efficient template rebinding and this is investigated. Here ITO-coated optical fibres were used, together with LMR as means of detection. Hence the analysis has focused on the wavelength shift associated with a change in refractive index i.e., through the addition or removal of nitroglycerin. This paper discusses the research challenges taking this approach to the detection of nitroglycerin, and in addition discusses the application to optical fibre sensing, to create an effective sensor for nitroglycerin detection. A non-imprinted polymer (NIP) is also created as a control measure and to compare with the performance of the MIP.

On waveguides covered with adsorbing nanostructures, various types of electromagnetic resonances can be achieved. One of these is lossy mode resonance (LMR). This occurs when the real part of the permittivity of a thin layer is positive and has a higher magnitude than its imaginary part and the permittivity of the surrounding medium (both the waveguide and the external medium) simultaneously. One material that meets the conditions for the occurrence of LMR is thin ITO, used as layers. The complex relative permittivity ϵ_m of the thin ITO layer is mostly modelled using the Drude model, which takes the form $\epsilon_m = \epsilon_\infty - \omega_p^2/(\omega^2 + i\Gamma\omega)$, where ϵ_∞ is relative permittivity for infinite frequency, ω_p is plasmon frequency and Γ stands for constant of relaxation⁶. Since ITO is not a metal, it holds that $\epsilon_\infty \neq 1$. The applications of LMR-based sensors are diverse; they can be used to measure refractive index, voltage, pH, humidity, the presence of chemical substances, antigens, or as biosensors⁷.

1. METHODOLOGY

As a substrate for ITO coatings, a 15-cm-long multimode polymer-clad silica fibres with a 400/730 μm core/cladding diameter were used. The cladding had a length of 20 mm removed from one sample which was previously polished, where the distal end was silver film coated. Following that, magnetron sputtering of ITO was carried out in the high-vacuum chamber, capable of reaching a base pressure of 10^{-5} Pa (thus ensuring high purity of deposition). A commercial, planar 3-inch magnetron equipped with a compound ITO target (an $\text{In}_2\text{O}_3/\text{SnO}_2$ composition of 90/10 wt% and a purity of 99.99 %) was used, and the distance between the fibre sample and the target was kept at 16 cm. The fibre sample was rotated during the deposition to obtain a uniform ITO coating around it.

After this, the stripped part of the fibre was coated with a xerogel, which was used as a layer to adhere the MIP coating to the optical fibre. The xerogel was made using tetraethyl orthosilicate 98% (TEOS), ethanol and deionized water, which were mixed using a magnetic stirrer, and the pH of the solution was checked periodically using litmus paper. As necessary, the pH was adjusted using small volumes of 0.1 M hydrochloric acid (HCl), and retested, adjusted to a slightly acidic pH (pH 4). The stripped section was then dipped into the xerogel solution for 1 minute, before being removed and left to dry overnight in a vertical position.

Following this, the same section of fibre was coated with the pre-polymerization solution. The process of making MIPs is discussed in some detail in the literature (and thus not repeated here), with a few key components: the template (analyte of interest of be detected); functional monomer (creates the polymer structure complementary to the template); crosslinker (further stabilizes the monomer); the solvent (dissolves all relevant components) and finally, the initiator (which initiates polymerization). The pre-polymerization solution is thus as follows: nitroglycerin, methacrylic acid, trimethylolpropane trimethacrylate (TRIM), ethanol and 2,2-dimethoxy-2-phenylacetophenone (photoinitiator). The solution was purged using argon (99.999% purity) at constant flow for 15 minutes. The solution was then transferred into a glovebox under argon atmosphere. The fibre was dipped into the pre-polymerization solution for 2 minutes, before being exposed to UV light for 5 minutes to initiate polymerization. In the results described below, this was repeated 3 times. The NIP pre-polymerisation solution was prepared in the same way, excluding nitroglycerin. To analyze the sensor performance, it was connected to a halogen light source and an Ocean Optics USB2000 mini spectrophotometer to detect the resultant spectrum.

2. RESULTS AND DISCUSSION

As the wavelength shift was directly impacted by the change in refractive index on the surrounding environment of the ITO-coated fibre, this wavelength shift was measured after each coating stage, for comparison, for both the MIP and NIP. Both were then immersed in a washing solution (9:1 methanol:acetic acid). In Figures 1(a-c), the results for the MIP sensor are shown, and a result for the NIP sensor in Figure 1d.

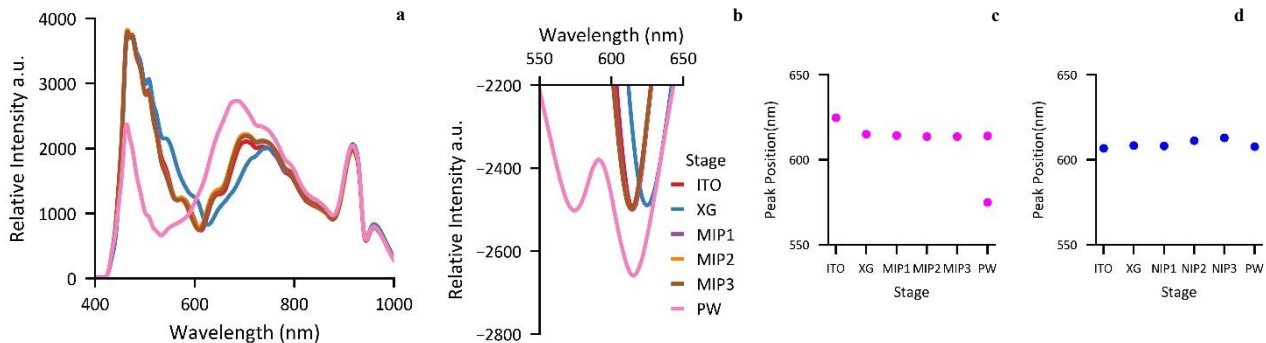


Figure 1. (a) Initial spectrophotometry data, normalized to match the resonance of each spectrum to the one resonance peak of the reference (reference not shown). (b) Wavelength shift of the different coating stages: ITO coating (ITO), xerogel (XG), 1 (MIP 1), 2 (MIP 2) and MIP (3) layer(s) of MIP, and post washing (PW) – data processing subtracts the reference and is normalized to the same intensity. (c and d) Scatter plot of how the peak position shifts with different coatings – where (c) is for the MIP and (d) NIP. The analyses were measured in air.

In Figure 1(a), a distinct shift can be seen between the position of the peaks compared to that post-washing (PW) – shifting to around 575 nm – the result of removing nitroglycerin from the MIP during the wash process. Two peaks appear from the post-washing measurement, one at around 615 nm and the other 575 nm. The reason for this, seen in Figure 1(a), is that there is a general shift of the entire spectrum towards the shorter wavelengths (left), noting a changed shape of the PW spectrum compared to the other analyses – as Figure 1(b) was created by removing the reference signal, this could explain the second peak, post-washing. The same analysis was also performed on the NIP. In Figures 1(c) and (d), the peak positions for the peaks are plotted over the coating stages; when comparing 3 layers of MIP/NIP to the situation post-washing, there was a shift of 5.19 nm (NIP) compared to 38.62 nm (MIP). This blue shift indicates a drop in refractive index PW, which corresponds to the removal of nitroglycerin from the MIP. The NIP also shifts slightly – some functional monomer or crosslinker molecules do not strongly bind to create the template-polymer complex and therefore are also washed out during the washing process – consequently, a wavelength shift would occur in both the MIP and NIP results.

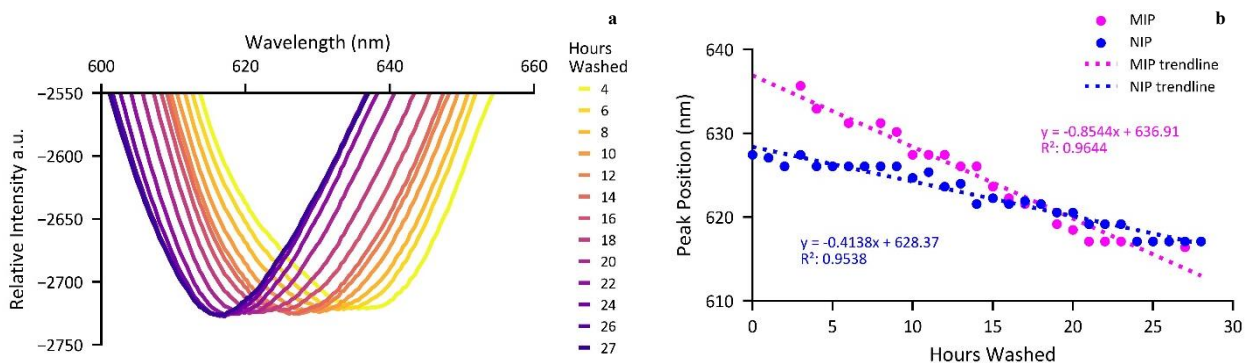


Figure 2. (a) Analysis of the MIP peak wavelength shift over time, relative to the reference output from the light source, immersed in the washing solution. Data was normalized to account for intensity changes from evaporation during washing. (b) Comparison of the peak wavelength shift over time of the MIP and NIP, following the analysis in Figure 2(a).

The effect of the washing process was investigated in detail, in that way to identify the point at which NG was removed, and the same process was performed on the NIP – the results are seen in Figures 2(a) and (b). Previous work had centred on washing the MIP and removing the template, before immersing the sensor into a template solution and analyzing the shift. This was seen to account for the absence in initial data points in the MIP in both Figures 2(a) and (b), as in the initial

stages, it was first washed for 4 hours, a measurement made every 2 hours, prior to immersing the sensor in the solution fully for 24 hours, then measuring every hour. The analysis shown in Figure 2(a) was also reproduced for the NIP – the results are shown in Figure 2(b).

Mirroring Figures 1(a-d), Figure 2(a) shows the gradual blue shift throughout the washing process. In Figure 2(b), both the MIP and NIP show wavelength shifts throughout the washing process, settling at a constant peak position at around 21 (MIP) and 24 (NIP) hours. However, the MIP response exhibits a sharper slope than that of the NIP – the MIP has trapped the nitroglycerin, therefore leading to its increase in wavelength as the refractive index is higher. The NIP, on the other hand, has an absence of NG, resulting in a gradual change of the slope. Considering the concentration of additional components were the same, it is logical that both the MIP and NIP both have the same final peak wavelengths. This is only apparent whilst in the solution, possibly down swelling in the gaps created in the MIP; as discussed previously, when analyzed in air, the MIP demonstrated a greater wavelength shift post-washing compared to that of the NIP.

3. CONCLUSIONS

In summary, this paper has demonstrated the promise of the MIP-OFS combination for use as a sensor system to detect NG and its quantitative capability, building on the considerable wavelength shift seen when removing NG. As a result, follow up analyses include reintroducing NG to the sensors presented and measuring the wavelength shift to establish the extent of reusability and thus determine the limit of detection. Further investigations to expand on the results in this paper have started, using Raman spectroscopy and other analytical techniques to characterize samples before and after template removal. This work is part of a wider investigation to use this device as a vapour generator, for the purpose of creating explosive vapour certified reference materials.

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