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Explosives detection by fluorescence quenching of conjugated polymers in suspended core optical fibers

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Abstract: In this work we demonstrate a suspended core microstructured optical fiber-based sensor platform for explosives detection based on the fluorescence quenching of a surface-attached conjugated polymer poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV). These fibers allow for strong evanescent field interactions with the surrounding media because of their small core size, and can sample minute liquid volumes. This is the first demonstration of a fluorescent conjugated polymer sensor capable of measuring liquid explosives samples loaded within an optical fiber. This technique is used to identify 1,4-dinitrobenzene (DNB), a member of the nitroaromatics family of explosives, in acetone for concentrations as low as 6.3 ppm in a total sampling volume of 27 nL and to quantify its concentration using the fluorescence decay lifetime, requiring an analysis time of only a few minutes.

Keywords: Explosives detection; Fluorescence sensor; Optical fiber sensor

1. Introduction

Sensing of nitroaromatic explosives such as trinitrotoluene (TNT), dinitrotoluene (DNT) and picric acid (PA) in groundwater or seawater is of importance for detecting buried unexploded ordnance and for locating underwater mines[1,2]. There are also environmental monitoring applications for characterizing soil and groundwater contaminated by toxic TNT at military bases[3]. Many technologies have been employed for the detection of trace levels nitroaromatics explosives,for example ion mobility spectrometry (IMS)[4], Terahertz spectroscopy[5], Raman spectroscopy [6], molecularly imprinted polymers (MIP) [7] and fluorescence quenching methods[8]. Among these, fluorescence quenching sensing methods are promising for rapid and sensitive detection of explosives[9]. The mechanism of fluorescence quenching is based on photoinduced electron transfer from excited fluorescent molecules to analytes. The electron-deficient nitroaromatics explosives in particular are much stronger quenchers of the fluorescence of electron-rich chromophores than a number of possible quenching molecules, imparting a degree of selectivity to the detection mechanism[10,11]. Utilizing sensory polymer films coated on a planar substrate (e.g., glass plate) has become the common method of choice for fluorescence quenching explosive detection[8,9,12]. However, large sampling volumes are needed as the fluorescent film is immersed in the explosives solution[12] and remote sensing can't be implemented.

Fiber optic sensing systems for explosives detection, in contrast are portable, flexible, low-cost, and capable of accessing hard-to-reach areas over long distances [13].Microstructured optical fibers (MOFs) have the potential to dramatically improve the performance of fiber optic sensors based on fluorescence spectroscopy and have recently attracted considerable interest [14-16], since a significant portion of the guided light can be located in voids within the fiber that can be used to sample the surrounding medium

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[17].Suspended-core MOFs with relatively large air voids surrounding the core can serve as a convenient platform to enable close interaction with liquids loaded into the voids, with portion of the guided light located in these voids. Thus, suspended-core MOFs enable the development of small sample volume, flexible and cost-effective sensing architectures[18].

In this work , the conjugated polymer poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV)which shows good solubility in organic solvents and high luminescence quantum yield in solutions and neat films[22], was used as a fluorescence indicator and coated on the inside of voids surrounding the core of a suspended-core optical fiber. The fiber is made from lead-silicate (Schott F2HT) glass as it combines high transmission in the visible spectral range with high refractive index [19]. The high transmission in the visible is of particular advantage for biological and chemical sensing applications since it allows for the efficient excitation of a range of fluorophores (for example Ru^{+} for dissolved oxygen sensing at 477 nm [20]). The refractive index of F2HT glass ($n_0 = 1.62$ at 588 nm) is significant higher than that of silica glass ($n_0 = 1.46$ at 588 nm), which results in enhanced fluorescence capture fractions for nano to microscale core sizes [17].This paper reports, for the first time to our knowledge, the use of a suspended core optical fiber sensor to detect explosives dissolved in an organic solvent. The explosive nitroaromatic analyte, 1,4-dinitrobenzene (DNB), was used during this investigation as it is chemically similar to the explosive TNT and highly electron-deficient[23-24]. The fluorescence intensity was integrated after the F2 suspended core fiber filled with DNB in acetone within a few minutes, and an exponential decay curve was obtained. The decay time of the exponential curve was used to determine the concentration of DNB. The limit of detection is 6.3ppm and there repeatability of the system was also explored.

2. Materials and methods

2.1 Solutions preparation
MEH-PPV (number average M_n = 70,000 - 100,000) was purchased from Sigma-Aldrich. Solutions of the polymer were prepared at 0.5mg/mL concentrations in different organic solvents (chloroform, chlorobenzene and tetrahydrofuran). The absorption spectra of these solutions were measured by a spectrophotometer (Agilent Technologies Cary Series UV-Vis-NIR) and are shown in Figure 1.

Tetrahydrofuran (THF) was chosen as the solvent as the polymer solution shows a peak in its absorption spectrum centered at 486nm which matches the 488 nm peak of the Argon ion laser used in this work. In addition, the boiling point of THF ($66^{o}C$) is lower than Chlorobenzene ($132^{o}C$), making evaporation of the solution within the fiber voids faster. DNB solutions were prepared by dissolving 2 mg of DNB in 20 ml of acetone and further diluting down to 0.0003 mg/ml (3.8 ppm), 0.0005 mg/ml (6.3 ppm), 0.001 mg/ml (12.6 ppm) and 0.003 mg/ml (37.8 ppm) to obtain lower concentration samples.

2.2 Coating procedure
An F2HT suspended core fiber with core diameter of 1.6 μm, determined as the radius of a circle with the same area as the fibre core, produced in-house was used. Sensors were made by cleaving 20cm lengths of fiber and depositing polymer layers onto the air/glass interfaces by flowing fluorophore solutions through the air voids of the suspended core fiber using 20 psi pressure of nitrogen gas at room

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temperature[25]. The fibers were then annealed at 75 $^{\circ}$C for 6-8 hours to completely evaporate the solvent. The thickness of the coating was in the order of 20-40 nm, measured by scanning electron microscopy (SEM). Figure 2 shows the SEM image of a F2 suspended core fiber coated with MEH-PPV.

The uniformity of the polymer coating was estimated using a Typhoon 8600 variable-mode imager that creates a map of fluorescence intensity across the entire surface of a coated fiber sample, as shown in Figure 3 along with the extracted fluorescence intensity for a cross-section running along the length of the fiber. This measurement was performed using 532 nm excitation light and collecting through a 560 nm long-pass filter for a 16 cm piece of fiber. The fluorescence intensity variation is a result of changes in the polymer thickness, with a standard deviation for the fluorescence intensity along the length of the fiber of 34%. This calculation excludes the edges of the fiber, which were cleaved prior to actual measurements.

2.3 Experimental setup

Figure 4 shows the experimental setup used for fluorescence measurements. Continuous wave (CW) light from a 488nm Ar$^+$ laser was reflected off a long-pass filter (Semrock 488 nm long-pass Razor Edge Ultra steep) and coupled into the F2HT suspended core fiber using a 40x microscope objective. A Thorlabs MC-2000 optical chopper was used, set to a frequency of 1.5 kHz, in order to slow down the optical bleaching of the fluorophore. After cleaving to achieve good facet quality at the ends of the fiber, a 16 cm length of suspended core fiber was used, resulting in a total sampling volume of 27 nL(the diameter of the air void is about 6.4μm). When one end of the fiber was dipped into the sample, capillary forces drew the liquid into the voids along the length of the fiber. Fluorescence could be detected at either end of the fiber, although backward detection provided the convenience of single-ended devices and an improved signal-to-pump ratio[24]. The fluorescence signal from the fiber was collected in backscattering mode through the long pass filter and recorded during and after the filling process (~4 mins) by a fiber-coupled cooled-CCD spectrometer (Horiba Jobin-Yvon iHR320). Measurements were also performed on fibers filled with pure acetone to evaluate the background level of the system.

3. Results and discussions

3.1Fluorescence emission spectra

Figure 5 shows the fluorescence spectra when the fiber was exposed to 12.6ppm DNB throughout a standard measurement. The spectra show broad fluorescence from MEH-PPV with an emission peak at 565 nm as well as a sharp peak at 510 nm due to the Raman peak of F2HT glass. The polymer's fluorescence naturally decays slowly due to photo-induced oxidation [27] and the rate at which it does so when exposed to pure acetone was used as a baseline. After filling of the fiber with DNB solution the fluorescence intensity decreased at a faster pace as a function of exposure time due to quenching by the DNB molecules. For a 12.6 ppm solution of DNB in acetone, the decrease in fluorescence intensity after 60 s was 35% and after 210 s it had been further reduced by 61%.

3.2 Quantification and detection limits

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The fluorescence spectra were integrated across all wavelengths to extract a value for the integrated fluorescence intensity value at regular time intervals. The resulting plot of fluorescence intensity as a function of measurement time demonstrates a decay behavior, as shown in Figure 6 for a DNB concentration of 12.6 ppm. The data for the time-dependent fluorescence intensity $I(t)$ were fitted using a single exponential decay equation of the form

$$I(t) = I_0 \exp(-t/\tau) + c \qquad (Eq.\ 1)$$

where I_0 is the initial value of fluorescence intensity, τ is the fluorescence decay lifetime and c is an offset constant. As shown in Figure 6 this equation shows a good fit with the experimental data (R^2=0.996). Different concentrations of DNB are expected to result in different decay dynamics and hence different values of τ that can then be correlated to the DNB concentration.

Figure 7 shows the relationship between the fluorescence life time of the MEH-PPV coated fibers, calculated using Eq. 1, and DNB concentration in the range of 0 ppm (pure solvent) to 37.8 ppm. From this figure we can see that the detection limit of the system is 6.3 ppm (30 μM) which is comparable to the limits of detection of 30.1 and 40.7 μM for DNT and TNT respectively by using a fluorescent-labeled imprinted polymer[28]. In addition, changes in the absolute value of fluorescence intensity, i.e. as a result of laser power fluctuations, do not affect the quantification of explosives, resulting in a more robust and reliable senor than techniques that are more sensitive but rely on absolute fluorescence intensity changes[29]. Further enhancement to the lowest detection limit could be achieved by metal surface enhanced fluorescence[30], which ultilizes surface plasmon effects to enhance the fluorescence intensity of the fluorophores and make them resistant to photobleaching[31].

3.3 Reproducibility

Three pieces of fiber coated under identical conditions were exposed to the same concentrations of DNB in acetone (6.3 ppm) at room temperature for four minutes. The emission spectra were recorded and decay times were obtained by fitting the exponential curves, as shown in Table 1.

The standard deviation for the fluorescence lifetime values at the sensor's detection limit of 6.3 ppm for three pieces of fibers was 10.3% which allowed the system to easily distinguish between different concentrations of DNB in acetone. These fluctuations can be attributed to slight changes in the polymer coating layer thickness and uniformity along the length of the fiber between different samples (the variability in the coating process is apparent in Figure 3).

4. Conclusions

In this work we have successfully demonstrated a sensing platform combining a suspended core optical fiber with fluorescence quenching of conjugated polymers by nitroaromatic explosives. The fluorescence intensity from a suspended core fiber internally coated with MEH-PPV was recorded over a period of a few minutes after filling with DNB in acetone. By fitting the fluorescence intensity as a function of time with a mono-exponential decay equation the fluorescence lifetime was used to determine the concentration of nitroaromatic compound DNB. The system is capable of detecting DNB in solution with limits of detection of 6.3 ppm without relying on absolute fluorescence intensity

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changes but by analyzing the dynamics of fluorescence quenching. These results highlight suspended core fibers as sensors with great promise for small volume, real time identification and quantification of trace quantities of explosives in solvents.

Acknowledgments

Vitae

Fenghong Chu obtained her PhD degree in optical engineering from Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences in 2008. She is now working in Shanghai University of Electric Power as an associate professor. Her current research interests include optical fiber sensing and integrated optics.

Georgios Tsiminis completed a degree in Applied Physics at the National Technical University of Athens, Greece in 2004 followed by a MSc in Photonics and Optoelectronic Devices at the University of St Andrews and Heriot-Watt University in Scotland, UK. He then joined the Organic Semiconductor Optoelectronics group at the University of St Andrews for his PhD on organic semiconductor lasers where he continued working as a research fellow on UV-nanoimprint lithography. In 2011 Georgios joined the Institute for Photonics and Advanced Sensing at the University of Adelaide in Australia, working on explosives detection using microstructured optical fibers.

Nigel A. Spooner received B.Sc. and M.Sc. degrees in Physics from the University of Adelaide in 1980 and 1987 respectively, and a D.Phil. from the University of Oxford in the field of radiogenic luminescence in solids in 1993. In 1993 he joined the Australian National University to establish a Luminescence Laboratory utilising environmental radiation dosimetry for geochronological applications. In 2002 he joined the Defence Science and Technology Organisation, and is currently on secondment to the University of Adelaide as Professor, Luminescence. His research interests include applications of radiogenic luminescence and fluorescence to substance detection, materials characterisation, retrospective dosimetry and geochronology.

Tanya Monro is an ARC Georgina Sweet Laureate Fellow and Director of the Institute for Photonics and Advanced Sensing (IPAS) at The University of Adelaide. She is a Fellow of the Australian Academy of Science (AAS) and the Australian Academy of Technological Sciences and Engineering (ATSE). Tanya obtained her PhD at The University of Sydney (Bragg Gold Medal for the best

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Physics PhD in Australia in 1998). In 2000 she received a Royal Society University Research Fellowship at the University of Southampton (UK). Tanya has published over 500 papers and her research focuses on creating disruptive photonic sensing technologies.

Table caption

Table 1.Fluorescence decay lifetimes for three pieces of F2 fiber coated with MEH-PPV and exposed to 6.3ppm DNB in acetone for four minutes.

Figure captions

Figure 1. Normalized absorbance spectra of MEH-PPV in different organic solvents. The inset shows the molecular structure of MEH-PPV.

Figure 2. SEM image of the inner walls of a F2 suspended core fiber internally coated with MEH-PPV. The inset shows a wide-angle view of the same fiber.

Figure 3. Fluorescence intensity of a MEH-PPV layer coated around the core of an exposed core fiber as a function of fiber position. The inset shows the raw image from the Typhoon imager for 532 nm excitation and collection through a 560 nm long-pass filter.

Figure 4. Experimental setup for detection of DNB in acetone solutions using MEH-PPV coated suspended core optical fibers.

Figure 5. Time-dependent fluorescence spectra (excitation at 488 nm) of a F2HT suspended core fiber internally coated with MEH-PPV after exposure to a 12.6 ppm DNB acetone solution at room temperature.

Figure 6. The integrated fluorescence intensity from a suspended core fiber internally coated with MEH-PPV after exposure to a 12.6ppm DNB solution for four minutes.

Figure 7. Fluorescence decay lifetime of MEH-PPV coated suspended core optical fibers for different concentration of DNB in acetone.

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Sample number	1	2	3	Average	Std. dev.
τ (s)	99.9	82.3	86.6	89.6	9.2

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Highlights

- Suspended core microstructured optical fiber explosives sensor in nanolitre volumes

- Suspended core coated with conjugated light-emitting polymer MEH-PPV

- Sensing based on fluorescence quenching dynamics

- Identification and quantification of nitroaromatic explosives

- Detection limit of 6.3 ppm for 1,4-dinitrobenzene (DNB) in acetone solution

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$$I(t) = I_0 \cdot \exp(-t/\tau) + c$$

$$R^2 = 0.996$$