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Optical-fiber arrays for vapor sensing

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ABSTRACT

This paper reviews the use of optical fibers as a platform to fabricate vapor sensitive arrays that have been developed in the authors' laboratory in recent years. Two types of fluorescence-based optical-fiber array systems are described: polymer-coated single core optical fibers and imaging fiber-optic bundles incorporating functionalized microspheres. Each system responds to an analyte vapor in a cross-reactive manner generating a multi-dimensional signal that can be used to train a pattern recognition program to identify subsequent exposures of the array to learned vapors. Several applications are described including explosives and nerve agent detection as well as the detection of several volatile organic compounds and ignitable liquids.

1. Introduction

Nature provides examples of two distinct frameworks for sensing target compounds in the environment. One approach is based on a 'lock-and-key' model where a single target compound is detected by a specific and non-cross-reactive receptor. This approach, exemplified by the specific binding between antibodies and antigens or between a protein receptor and its ligand, has been successfully exploited by synthetic sensing systems for the detection of numerous chemical species. Analytical sensors employing a lock-and-key design generate an analytical signal only when the target species is present. Any reactivity with another chemical species is problematic as it will result in a response that is registered as an interference. This approach requires that a specific sensor be created for every new target to be detected. Natural systems have developed a repertoire of such receptors to adapt to a complex and ever changing environment. This breadth of specificity has been difficult to reproduce in artificial systems due to the synthetic burden of generating an absolutely specific sensor for every desired analyte and the challenge of compiling them into a platform that scales to detect a large number of targets.

A second sensing strategy employed by nature consists of a more general approach and is exemplified by mammalian olfactory systems. It has been estimated that mammals are capable of detecting and discriminating tens of thousands of odorant molecules spanning an immense range of chemical diversity [1]. What is fascinating about the olfactory system is that this broadband sensitivity is accomplished using many fewer receptors than the number of odors that can be detected [2,3]. Furthermore, olfactory systems constantly evolve over the lifetime of the organism by incorporating new odors into memory. Biological studies have demonstrated that many olfactory receptors respond when an odorant is encountered [3–5]. This type of multi-receptor triggering is referred to as cross-reactivity and the signals from numerous cross-reactive sensors are processed to create a multi-dimensional response that is perceived as a particular odor [6–8]. Specificity is therefore encoded in the overall pattern of responses from all the receptors rather than being a function of any single specific receptor as in the conventional ligand–receptor strategy. Despite the fact that odor receptors have a typical lifetime of a few weeks, odor memories persist throughout the life of the organism indicating a transfer of information over time with receptor turnover.

Artificial or electronic nose systems are analytical devices based loosely on the sensing approach employed by biological olfactory systems. They incorporate arrays of cross-reactive and semi-selective sensors that respond collectively when exposed to a particular odorant or an odorant mixture. The aggregate response from all of the sensors in the array comprises a unique pattern that can be used to train a classification algorithm to recognize subsequent exposures of the array to a particular vapor. Numerous platforms have been developed that incorporate a wide range of different transducers including, field-effect devices [9], chemiresistors [10,11], surface acoustic wave devices [12], colorimetric detection [13,14], and mass spectrometers [15]. These devices can be tailored in their classification depending on the application; for example, ethanol can be classified as 'ethanol' just as easily as it can be classified as 'alcoholic'. In the same way that biological systems struggle with quantification, expressing concentrations in arbitrary terms such as 'strong' or 'weak', artificial nose systems have similarly struggled to express concentrations in absolute terms. In spite of this drawback, artificial nose systems have shown promise when applied to analytical tasks where rapid qualitative measurements

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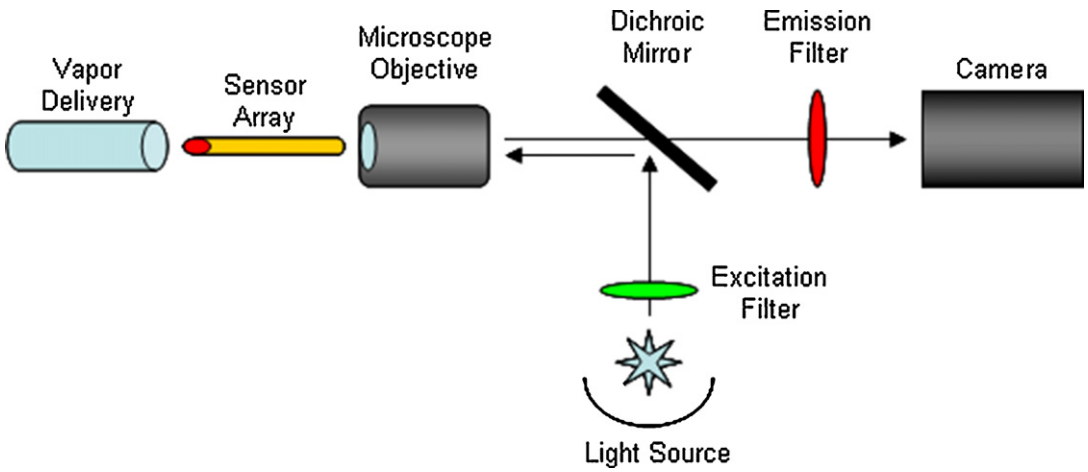

Fig. 1. Schematic of the instrumental apparatus used for the fluorescence-based optical-fiber array artificial nose. Analyte vapors are pulsed to the sensor array through the terminus of the vapor delivery line. Sensor responses are recorded during the vapor exposure using either a CCD or CMOS camera.

are needed. In this paper, we review our work in the area of optical-fiber based artificial nose systems.

2. Optical sensor arrays

In our laboratory, we have developed a fluorescence-based artificial nose system that incorporates fiber-optic sensors as the vapor sensitive elements. These types of sensors, in general, consist of bundles of fibers or fiber-optic arrays that are functionalized with analyte sensitive materials at their distal ends [16,17]. The analyte sensitive materials typically contain an indicator that changes its optical properties when a target compound is present. In our artificial nose system, we have created cross-reactive sensors by immobilizing several solvatochromic fluorescent dyes in a variety of polymer and monolayer phases. Excitation light is directed into the optical fiber at the proximal end where it is guided, via total internal reflection, to the immobilized indicator. The fluorescence from these sensors is isotropically emitted and is collected and transmitted back through the optical fiber where it is detected using conventional photodetectors such as charge-coupled device (CCD) or complementary metal-oxide-semiconductor (CMOS) cameras. A schematic of the system used to collect sensor responses is presented in Fig. 1. We have implemented two distinct types of optical-fiber sensors in our artificial nose system: polymer-coated single core fibers and microsphere-based vapor sensitive arrays.

2.1. Polymer-coated single core optical-fiber sensors

Our initial experiments employed the solvatochromic dye Nile Red immobilized in a variety of thin film (50–100 μm) polymer layers attached to the distal ends of single-core optical fibers [18–22]. The polymer phases were applied by dissolving the polymer and Nile Red in a cosolvent and dip-coating the distal end of an optical fiber. The fluorescence maximum of Nile Red changes depending on the polarity of the environment immediately surrounding the dye [23–26]. Each polymer phase establishes a baseline microenvironment that fixes the initial fluorescence maximum of the sensor. When the sensor is exposed to an analyte vapor, the vapor partitions into the polymer and changes the polarity of the microenvironment surrounding the dye molecules. This polarity change produces a shift in the fluorescence wavelength maximum and/or the emission intensity of the indicator dye. This change in the fluorescence characteristics of the sensor is further affected by the concentration of analyte vapor, the rate at which the vapor partitions into the polymer layer, and the change in excitation light coupling into the sensing layer due to polymer swelling. By varying the composition of the polymer phase over several fibers, a diverse set of sensors exhibiting different signals can be produced [27].

Several individual fibers, each coated with a different polymer phase, were bundled together to form an array of sensors that could be simultaneously monitored. An ensemble of sensor responses from this type of array to toluene vapor is presented in Fig. 2. This diverse set of fluorescent signals encompasses the change in emission intensity of the dye over time as the analyte vapor is presented to the array. These responses are highly reproducible over subsequent exposures of the array to the same vapor [19]. When the array is exposed to different concentrations of the same vapor, the magnitude of the sensor responses changes but the general shape of the responses is maintained [20]. The array responds quickly and most sensors reach their maximum change from baseline within a few seconds after the vapor has been presented. When examined *in toto*, the array responds uniquely to each vapor and these responses can be compiled into a training database and used to build a classification model with a pattern recognition algorithm. When an unknown vapor is presented to the array, the response is analyzed using the algorithm and the identity of the unknown vapor is assigned by comparison to the known responses in the training database. Early pattern recognition programs consisted of artificial neural networks that were constructed using integrated sensor responses [18,19] as well as a compilation of descriptors derived

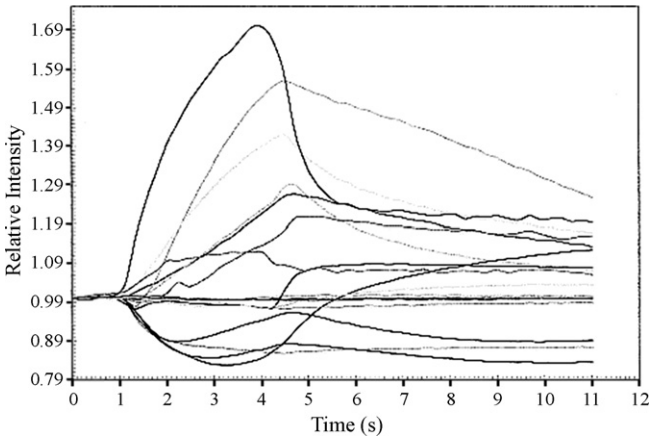

Fig. 2. The responses of an array of 19 polymer-coated single core sensors to a single pulse of saturated toluene vapor. Reprinted from Ref. [22] with permission from Elsevier.