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ScienceDirect
Sensors and Actuators B 130 (2008) 758–764
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

Enhanced oxygen detection using porous polymeric gratings with integrated recognition elements

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Received 14 February 2007; received in revised form 13 October 2007; accepted 23 October 2007
Available online 17 November 2007

Abstract

The development of ordered porous nanostructured materials, such as polymeric Bragg gratings, offers an attractive platform for the encapsulation of chemical and biological recognition elements. To date, various types of polymer gratings have been developed with several demonstrated applications in switching, lasing, and display devices. Here, we focus on a new class of holographically ordered porous polymer (HOPP) gratings that are an extension of holographic polymer dispersed liquid crystal (H-PDLC) structures. We present biochemical sensing using HOPP gratings that include a volatile solvent as the phase separation fluid. The resulting HOPP gratings are simple to fabricate, chromatically tunable, highly versatile, and can be employed as a general template for the encapsulation of recognition elements. As a prototype, we developed an oxygen (O_2) sensor by encapsulating the fluorophore (tris(4,7-diphenyl-1,10-phenathroline)ruthenium(II) within these nanostructured materials. The resulting O_2 sensors performed across the full-scale range (0–100%) of oxygen in nitrogen, with a response time of less than 1 s. The O_2 sensor system uses a LED excitation source and a silicon photodiode detector. The ability of these HOPP reflection gratings to transmit or reflect a particular wavelength range, based on the grating spacing, enables us to selectively enhance the detection efficiency for the wavelengths of interest.
Published by Elsevier B.V.

Keywords: HPDLC gratings; Porous structures; Fluorometry; Optical sensors; Reflection gratings; Nanostructured sensors; Oxygen sensors; Biosensors; Biochemical sensors

1. Introduction

Nanostructured materials are playing an increasingly important role in the advancement of optical science and technology in various application areas including light emitting devices, biomedical diagnostics and imaging, sensing, information storage, and communications [1]. Here, we describe the development of sensors using nanostructured materials that act as an encapsulation template for biochemical recognition elements. This approach exploits unique optical properties of these structures. There have been numerous examples of chemical and biochemical sensors that have used nanotechnology to enhance sensitivity, selectivity, and dynamic response [2–6]. In this paper, we describe the development of nanosensors based on optical (fluorescence) sensing mechanisms. Fluorescence spectroscopy is a well-known and useful modality for highly selective and sensitive chemical and biochemical sensors [7]. Fluorescence based sensing offers several advantages including fast response times, easy implementation, and stand-off detection. Typically, fluorescence based sensors excite optically active recognition elements that are selective to particular analyte(s) of interest. Emission from the recognition element, at wavelengths longer than the excitation wavelength, is monitored and provides information regarding the concentration of the analyte(s). Thus, in this tech-

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0925-4005/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.snb.2007.10.073

nique, it is important to (i) immobilize the recognition element at the sensor surface and (ii) maximize the contact surface area to maximize interaction of the analyte with the recognition element during the sensor operation.

Porous materials are well suited for the encapsulation and immobilization of optically active recognition elements while providing maximum surface interaction area. Sensors based on porous materials can use the changes in the optical resonances that occur when the porous structures are occupied by the analyte species, thus enabling a simple and effective detection mechanism [8,9]. Porous silicon structures provide an excellent example of effective use of porous materials for sensing [10,11]. Although porous silicon provides an effective platform, there is significant interest in extending these concepts to polymeric materials because of their comparatively easy fabrication process, cost effectiveness and mechanical flexibility. For example, nanoporous polymer replicas have been produced from an oxidized porous silicon template for sensing applications [12]. In addition, micropatterned polymeric grating structures have been demonstrated as a platform for recognition elements [13].

In this work, we report the use of porous polymeric photonic bandgap structures (Bragg reflection gratings) with an oxygen (O_2) sensitive recognition element incorporated directly within the polymeric structure. This composite sensing structure is fabricated with a simple one-step holographic method that uses a non-reactive solvent, formamide, as the phase separation fluid. Specifically, the porous polymer gratings are formed when the pre-polymer syrup containing a monomer, a photoinitiator, a co-initiator, a cross-linking monomer and formamide (a volatile, polar solvent) is sandwiched between two microscope slides, and exposed to an interference pattern generated from a simple one-beam laser setup as previously reported [14,15]. This simple fabrication process produces wavelength tunable reflection gratings (one-dimensional (1D) photonic bandgap structures). In addition, by a simple modification of the experimental apparatus, to add additional laser beams, 2D and 3D porous photonic bandgap structures can be produced. This paper describes only the fabrication and implementation of sensing elements using reflection gratings. This fabrication method provides several advantages for production of multifunctional components: (1) controlled porosity by varying the composition of the pre-polymer syrup and experimental conditions; this property is important for accommodating a variety of compounds into the pores and providing easy access of the analyte into the pores, (2) selective enhancement of the detection efficiency for the wavelengths of interest by varying the grating spacing, (3) simple and inexpensive starting materials and (4) rapid fabrication. In addition, the resulting structures are stable for extended periods of time (months).

Previously, we have demonstrated the ability of the reflection grating structures to sense volatile organic compounds (VOCs) such as acetone, methanol, pyridine, and toluene. The reflection spectra (color) of the reflection grating shifted as the VOC vapors penetrated the voids in the grating structures and the resulting wavelength shift was measured using wavelength sensitive photodetectors [16,17]. Unfortunately, those gratings provided limited selectivity. The current work serves to demonstrate the ability to use these reflection grating structures as a generic template for the encapsulation of recognition elements to sense a variety of analytes such as biochemicals, toxins, pollutants, and biomarkers. As a prototype, we present an O_2 sensor by encapsulating the fluorophore (tris(4,7-diphenyl-1,10-phenathroline)ruthenium(II) ($[Ru(dpp_3)]^{2+}$) within these porous materials. This O_2 sensor operates by monitoring the reduction of the fluorescence intensity as the O_2 concentration increases due to collisional quenching [18,19]. The reflection gratings are multifunctional in that they provide a template for encapsulation of the recognition element while providing controllable optical properties that can minimize the required elements in fluorescence based sensors. As explained earlier, fluorescence based sensors encode the information regarding the analyte concentrations in the emission response from the fluorophores at wavelengths longer than the excitation light. Thus, in practical applications, a discrete optical long-pass filter is required to ensure that the optical excitation does not saturate the photodetector. Thus, the prototype sensor presented in this paper demonstrates a template for self-contained planar sensor structures with controllable optical properties. Specifically, the sensor is a fluorescence-based sensor with integrated filtering of the excitation source.

2. Fabrication of porous polymer reflection gratings sensors

2.1. Preparation of the pre-polymer syrup with oxygen recognition elements

The pre-polymer syrup for the reflection gratings includes an acrylate monomer (dipentaerythritol penta-/hexa-acrylate (DPHPA) from Aldrich), a coinitiator (*N*-phenylglycine (NPG) from Aldrich), a photoinitiator (Rose Bengal (RB) from Spectra Group Ltd.), a reactive solvent (1-vinyl-2-pyrrolidone (NVP)), and a surfactant (docusate sodium salt (AOT) from Aldrich). The reactive solvent, NVP, is used to reduce the viscosity of the monomer and to ensure the homogeneity of the pre-polymer syrup. In addition, NVP helps to dissolve the photoinitiator and co-initiator and is also involved in the chemical reaction as a cross-linking agent. Finally, a polar volatile solvent, formamide, is added to the pre-polymer syrup. The composition of the pre-polymer syrup is 1 wt.% NPG, 0.5 wt.% RB, 25 wt.% NVP, 6.5 wt.% AOT, 42 wt.% DPHPA, and 25 wt.% formamide. A mixer (Vortex Genie 2, G-560) is used to homogenize the syrup. For O_2 recognition elements, the following reagents are also used: O_2 sensitive fluorophore: tris(4,7′-diphenyl-1-10′-phenathroline) ruthenium(II) chloride pentahydrate ($[Ru(dpp)_3]Cl_2{\cdot}5H_2O$) from GFS Chemicals, and ethanol (EtOH) from Quantum Chemical. The $[Ru(dpp)_3]^{2+}$ is purified as described in the literature and $[Ru(dpp)_3]^{2+}$ (1 mg) is dissolved into ethanol (10 mg) [20]. Finally, the O_2 recognition elements are added and mixed into the previously prepared pre-polymer syrup with 1:4 ratio. A few drops (approximately 50 μl) of this pre-polymer syrup are sandwiched between two clean microscope slides.