Full length article

Porphyrin-nanoassembled fiber-optic gas sensor fabrication: Optimization of parameters for sensitive ammonia gas detection

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A B S T R A C T

Highly sensitive fiber-optic ammonia gas sensors were fabricated via layer-by-layer deposition of poly(diallyldimethylammonium chloride) (PDDA) and tetrakis(4-sulfophenyl)porphine (TSPP) onto the surface of the core of a hard-clad multimode fiber that was stripped of its polymer cladding. The effects of film thickness, length of sensing area, and depth of evanescent wave penetration were investigated to clearly understand the sensor performance. The sensitivity of the fiber-optic sensor to ammonia was linear in the concentration range of 0.5–50 ppm and the response and recovery times were less than 3 min, with a limit of detection of 0.5 ppm, when a ten-cycle PDDA/TSPP film was assembled on the surface of the core along a 1 cm-long stripped section of the fiber. The sensor's response towards ammonia was also checked under different relative humidity conditions and a simple statistical data treatment approach, principal component analysis, demonstrated the feasibility of ammonia sensing in environmental relative humidity ranging from dry 7% to highly saturated 80%. Penetration depths of the evanescent wave for the optimal sensor configuration were estimated to be 30 and 33 nm at wavelengths of 420 and 706 nm, which are in a good agreement with the thickness of the 10-cycle deposited film (ca. 30 nm).

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1. Introduction

Fiber-optic sensing techniques have attracted a great deal of attention in a variety of analytical areas such as chemical and biological sensing [1,2], environmental monitoring [3], and medical diagnostics [4]. In general, the capabilities of the sensing platforms are well-understood, and it is the availability of appropriate functional coatings that is considered to be the key factor in providing the amplification of the sensitivity and selectivity of sensors towards target analytes that is required for the development of efficient fiber-optic sensors. The creation and development of sensitive materials that can be provide measurable perturbation of the optical signals will expand the application area of fiber-optic sensors. The following characteristics are generally required for the fabrication of sensitive and selective fiber-optic sensors [5]: transparent in appropriate spectral ranges, specific optical changes under the influence of chemical species, fast and reversible response, wide dynamic range, easy immobilization and cheap manufacturing.

Various coating techniques, such as dip- and spin-coating [6,7], layer-by-layer (LbL) deposition or electrostatic self-assembly [8], Langmuir-Blodgett deposition [9] and chemical and physical vapor deposition [10,11] have been employed for functionalization of optical fibers. Among these techniques, the LbL technique, which is based on the alternate adsorption of polycations and polyanions onto solid substrates [12–14], has been shown to a powerful surface modification method. This alternate deposition technique is still expanding its potential because of its versatility and convenience for the fabrication of nanoassembled thin layers employing various organic and inorganic materials.

Ammonia is one of the major metabolic compounds and the importance of its sensitive detection has been emphasized recently because of its correlation with specific diseases [15–22]. At normal physiological conditions, ammonia can be expelled from the slightly alkaline blood and emanated through the skin or exhaled with the breath. Dysfunction in the kidney or liver that converts ammonia to urea can result in the increase of the ammonia concentration in breath or urine. Consequently, the detection of the

ammonia present in breath or urine can be used for the early diagnostics of liver or stomach diseases [16]. The development of sensor devices for measuring ammonia with a sensitivity of 50–2000 ppb and with a fast response time is highly desired [15].

Conventional methods for ammonia detection are based mainly on gas chromatography-mass spectrometry (GC–MS) [16], which, despite its high selectivity and sensitivity, is expensive and time-consuming and requires a well-trained operator. In particular, it is known that real sample measurements must be conducted at high relative humidity (RH) levels (>90%) [15]. Cheap, small, sensitive, and reliable sensor devices that can efficiently operate at different RH levels could facilitate the creation of point-of-care medical systems that could be used in daily life.

In this regard, optical fiber sensors provide an excellent platform for the development of low cost, small, sensitive, and reliable ammonia sensors. In the past decades various fiber-optic sensing platforms utilising different sensitive layers have been used to develop ammonia sensors. The first-reported fiber-optic ammonia sensor, proposed by Wolfbeis, employed the measurement of fluorescence from a pH indicator solution [23]. Since then, a range of optical fiber-based ammonia sensors have been reported, including lossy mode resonances [24], evanescent wave spectroscopy [25–27], end-reflection, where the sensing element is at the tip of the fiber, [28,29] and in-fiber gratings [30]. Generally, the sensitivity of these devices ranged from 10 s to 100 s of ppm. Table 1 summarizes the parameters of a selection of the ammonia sensors reported in the literature.

In our previous work, we have demonstrated an intrinsic fiber-optic gas sensor with an alternate film of poly(diallyldimethylammonium chloride) (PDDA) and tetrakis(4-sulfophenyl)porphine (TSPP) [31]. The exposure of the nanoassembled film to ammonia induced unique optical changes in the transmission spectrum of the optical fiber, reflecting the characteristic absorption bands (Soret and Q bands) of the assembled TSPP compound.

In this study, the influence on sensor performance of film thickness, the length of sensing area and the penetration depth of evanescent wave are examined in more detail. In addition, the effects of RH, one of the major interference factors in real-life measurements, was thoroughly studied. The sensor's response to ammonia of various concentrations was measured at different RH levels and the results have been statistically analysed via principal component analysis (PCA).

2. Experimental

2.1. Materials

TSPP (Mw: 934.99) and sodium hydroxide (NaOH) were purchased from Tokyo Kasei (Tokyo, Japan). PDDA (Mw: 200,000–350,000, 20 wt% in H$_2$O) was purchased from Sigma–Aldrich (St. Louis, USA). The TSPP and PDDA chemical structures are shown

in Fig. 1. A HCS200 multimode optical fiber, with a silica core and a plastic cladding of diameters 200 μm and 400 μm, respectively, was purchased from Ocean Optics (Largo, USA). Standard ammonia gas of concentration 100 ppm in dry air was purchased in cylinder from Japan Air Gases (Kitakyushu, Japan). Pyridine and toluene, used as additional analyte gases, were purchased from Wako Pure Chemical Industries (Osaka, Japan). All of these chemicals were of analytical grade, and they were used without further purification. Deionized pure water (18.3 MΩ cm) was obtained by reverse osmosis followed by ion exchange and filtration using a Direct-QTM (EMD Millipore, Billerica, USA).

2.2. Optical fiber preparation

The details of the electrostatic LbL technique employed for the deposition of a porphyrin nanoassembled thin-film onto an optical fiber are described elsewhere [30,31]. Briefly, prior to film deposition, a short section of the plastic cladding was burned off the fiber. The exposed section of the silica core was rinsed in ethanol and deionized water for several times and treated with 1 wt% of ethanolic KOH (ethanol/water = 3:2, v/v) for 20 min to functionalize the surface of the silica core with OH groups. The fiber core was then rinsed with deionized water and dried by flushing with nitrogen gas. Thin-films were prepared by alternately immersing the fiber into PDDA (0.5 wt% in water, pH 7.8) and TSPP (1 mM in water, pH 4.6) solutions for 15 min each, thereby producing a PDDA/TSPP bilayer. This was achieved by introducing a coating solution (volume 150 μL) into a deposition cell with intermediate processes of water washing and drying by flushing with nitrogen gas being undertaken, as illustrated in Fig. 1. The resulting film is denoted by (PDDA/TSPP)$_x$, where x indicates the number of deposition cycles. To check the effect of the film thickness, 5-, 10-, and 15-cycle films were deposited on the activated core of the optical fiber and in every case the outermost surface of the alternate film was TSPP.

One end of the optical fiber was connected to a deuterium-halogen light source (DH-2000-Ball, Mikropack), while the other end was connected to a spectrometer (S1024DW, Ocean Optics) to monitor the assembly process. The absorbance was determined by taking the logarithm of the ratio of the transmission spectrum of the coated fiber, $T(\lambda)$, to the transmission spectrum measured prior to film deposition $T_0(\lambda)$.

$$A(\lambda) = -\log[T(\lambda)/T_0(\lambda)], \tag{1}$$

2.3. Optical measurement set-up

Desired gas concentrations were produced using a two-arm flow system, as shown in Fig. 2. A specially designed Teflon chamber was used to allow the sensor to be exposed to varying analyte concentrations [31]. The stripped section of the optical fiber,

Table 1
Summary of the ammonia sensor parameters.

Sensor type	Sensitive element	Lower detection limit (LoD)/lowest measured concentration (LMC)	Response time	Reference
Evanescent wave	Universal pH indicator	10 ppm (LMC)	5 min	[25]
	Bromocresol purple/bromocresol green, dip coating sol- gel	9 ppm (LMC) 0.014 dB/ppm	8 s	[27]
	Bromocresol purple, sol-gel	145 ppm (LMC)	10 s	[26]
Reflection type	ZrO$_2$/PSS nanoassembly	1 wt% (LMC)	Several min	[29]
	Oxazine 170 perchlorate	200 ppm (LMC)	–	[28]
Lossy mode resonance	Titanium dioxide containing TMPyP	0.1 ppm (LMC)	30 s	[24]
Grating based	PDDA/TSPP	0.67 ppm (LoD)	–	[30]