Development of a Prototype Optival Hydrogen Gas Sensor Using a Getter-Doped Polymer Transducer for Monitoring Cumulative Exposure: Preliminary Results

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Development of a Prototype Optical Hydrogen Gas Sensor Using a Getter-Doped Polymer Transducer for Monitoring Cumulative Exposure: Preliminary Results

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Abstract

A novel prototype optical sensor for monitoring cumulative hydrogen gas exposure was fabricated and evaluated. Chemical-to-optical transduction was accomplished by detecting the intensity of 670 nm laser light transmitted through a hydrogen getter-doped polymer film mounted at the end of an optical fiber; the transmittance of the composite film increased with uptake of hydrogen by the embedded getter. The composite film consisted of the hydrogen getter 1,4-bis(phenylethynyl)benzene, also known as DEB, with carbon-supported palladium catalyst embedded in silicone elastomer. Because the change in transmittance was irreversible and occurred continuously as the getter captured hydrogen, the sensor behaved like a dosimeter, providing a unique indication of the cumulative gas exposure.

Keywords: Gas sensor; Hydrogen getter; Optical fiber; Polymer

1. Introduction

The explosive and corrosive nature of hydrogen gas spurred the development of sensors [1] to indicate its presence. Most hydrogen sensors track the partial pressure of hydrogen, providing an indication of the current hydrogen level. They often rely on a transduction element incorporating a palladium-based outer layer. Palladium selectively catalyzes the dissociation of molecular hydrogen to atomic hydrogen, which can absorb reversibly into the transduction element. Various sensors based on hydrogen-induced changes in electrical [2,3], optical [4-7], and mechanical [8-10] properties of the palladium-based transduction element have been constructed. When the hydrogen exposure ceases, the original physical and chemical properties of the transduction element are recovered, and the sensor output returns to its baseline. Unless the sensor is operated and monitored continuously, transient gas exposures may be missed.

Unlike the transduction materials typically used in hydrogen sensors, materials known as irreversible hydrogen getters undergo a permanent change in chemical structure when exposed to hydrogen. Solid organic hydrogen getters, first developed at Sandia National Laboratories in the 1970's [11,12], permanently bond with hydrogen in the presence of a catalyst such as palladium. They were originally developed for, and have current application in, closed systems in which hydrogen out-gassing and/or generation can have deleterious effects on electronic components and/or reach hazardous levels [13-17]. Because the getter permanently bonds with hydrogen, the resulting changes in its physical and chemical properties are irreversible. A sensor employing a transducer comprised of a getter would provide a unique indication of the cumulative gas exposure, effectively acting like a dosimeter, which could complement the output of common hydrogen sensors. Potential applications include monitoring cumulative hydrogen exposure resulting from outgassing, chemical reaction, or diffusion. Such a device may be particularly useful for monitoring such processes in material aging or degradation studies. Because the hydrogenation of the getter is permanent, such a sensor would have a finite lifetime dependent on the uptake kinetics.

We investigated the use of the solid organic hydrogen getter 1,4-bis(phenylethynyl)benzene, also known as DEB, as a chemical-to-optical transduction material for a hydrogen sensor. This is the first reported instrumentation of a getter to enable gas sensing. As shown in Fig.1, DEB is an unsaturated hydrocarbon whose alkyne moieties (triple bonds between carbon atoms) become saturated alkanes (single bonds) when catalytically hydrogenated [18]. We present the formulation of a getter-polymer composite transduction element and report the effect of hydrogen exposure on its visible light transmittance. In addition, we describe the fabrication of a prototype optical fiber-based hydrogen sensor employing the getter-based transduction element and present the results of preliminary testing.

2. Experimental

2.1. Transducer fabrication and characterization

Chemical-to-optical transduction was accomplished by monitoring the intensity of light transmitted through a polymer film doped with a mixture of DEB and carbon-supported palladium catalyst (Pd/C). The ratio of DEB to Pd/C was 3:1 by weight, and the Pd/C component consisted of 5% palladium and 95% activated carbon by weight. The DEB-Pd/C mixture, a loose powder (maximum particle size = 74 µm) gray in color due to the Pd/C (pure DEB is colorless [19]), was provided by Kansas City Plant (Kansas City, Missouri, USA). Similar DEB-Pd/C-polymer composites demonstrating the ability to permanently capture hydrogen have been reported [13,14,20,21].

Formulation of the composite film began by further grinding the DEB-Pd/C powder using a mortar and pestle and then mechanically homogenizing it with a silicone elastomer base (Sylgard 184, Dow Corning Corp., Midland, Michigan, USA) to achieve uniform dispersion of the getter. After degassing, the Sylgard 184 curing agent was added (ratio of base to curing agent = 10:1 by weight) and the mixture was stirred and degassed again. The mixture was sandwiched between glass plates and cured at 60°C under nitrogen to form the film. The final film, shown in Fig. 2, was 125 µm thick and contained 10% DEB-Pd/C by weight. While the getter appears uniformly dispersed by eye, variation in particle size and clumping is evident on a microscopic scale. A biopsy punch was used to obtain a section of the film for use in the sensor. The hydrogenated sensor film was replaced with a fresh (virgin) section of film after each test.

Using the optical system [Fig. 3(a)], sensor unit [Fig. 3(b,c)], and gas flow system (Fig. 4) described below in Section 2.2, the transmittance of the getter composite film at a red wavelength of 670 nm was measured as a function of hydrogen exposure time. The mirror shown in Fig. 3(b) was not used for this experiment, opening a direct path for the gas to reach the film. The sensor unit containing the film was exposed to a gas mixture of 5% hydrogen by volume in argon at room temperature. The sensor unit was periodically removed from the flow system and the light transmitted through the film was measured using a power meter (LabMaster-E with LM-2 detector head, Coherent, Inc., Santa Clara, California, USA).

2.2. Sensor setup and testing

The optical system is shown in Fig. 3(a). A 670 nm, 4.2 mW diode laser (0220-986-00, Coherent, Inc., Santa Clara, California, USA), powered by a DC power supply (E3630A, Hewlett-Packard Co., Palo Alto, California, USA) at 5 V, was coupled into a multimode optical fiber using a fiber collimation lens (F220SMA-B, Thorlabs, Inc., Newton, New Jersey, USA). A fiber splitter directed half of the light to a photodiode (PDA55, Thorlabs, Inc.) to monitor the laser output. The rest of the light continued via a fiber to a seven-fiber bundle (C Technologies, Inc. Bridgewater, New Jersey, USA), where it was coupled into the central fiber. The 400 μm diameter central fiber (numerical aperture ≈ 0.2) delivered the light to the sensor unit, where it was collected by the surrounding six fibers (each 400 μm in diameter) in the bundle after passing through the getter composite film, reflecting from a mirror, and passing through the film a second time [Fig. 3(b)]. The collection fibers were split from the central fiber and directed to another photodiode (PIN-10DF, UDT Sensors, Inc., Hawthorne, California, USA). The photodiode current was amplified by a current amplifier (13AMP005, Melles Griot, Irvine, California, USA) to yield the sensor signal. The sensor signal was corrected based on the laser output to reference out laser intensity fluctuations. The sensor signal was recorded as a function of hydrogen exposure time at a rate of 0.1 Hz using LabVIEW software (National Instruments, Austin, Texas, USA). No data filtering or smoothing was performed.

The components of the sensor unit are illustrated in Fig. 3(b). The components were housed in a plastic fixture made in-house. The getter composite film was located at the end of the fiber bundle, followed by two plastic spacer rings and a 5 mm diameter silver mirror (Part NT49-186, Edmund Optics, Barrington, New Jersey, USA). The plastic spacer rings, which were made in-house using a milling machine (MDX 650, Roland DGA Corp., Irvine, California, USA), were designed to maintain a distance of 1.5 mm between the end of the fiber bundle and the mirror while allowing hydrogen gas to reach the getter composite film from the flow channels in the housing fixture. The fully assembled sensor unit is shown in Fig. 3(c).

A schematic of the gas flow system used to evaluate the sensor is shown in Fig. 4. A gas mixture of 5% hydrogen in argon was used. An Ultra-Torr vacuum fitting (SS-6-UT-1-4, Swagelok Co., Solon, Ohio, USA) was used to connect the sensor unit to the flow system. An Ultra-Torr reducing union (SS-6-UT-6-4, Swagelok Co.) was used to prevent leakage between the fiber bundle ferrule and the housing fixture. A flow controller (1179A Mass-Flo controller with PR4000 power supply, MKS Instruments, Inc., Wilmington, Massachusetts, USA) regulated the flow. After purging the system at a flow rate of approximately 200 cc/min, the flow was reduced to approximately 10 cc/min and held constant. Testing was performed at room temperature.

3. Results and discussion

3.1. Transducer transmittance

The 670 nm transmittance of the DEB-Pd/C composite film at increasing hydrogen exposure times is shown in Fig. 5. The transmittance increased relatively slowly with hydrogen exposure time during the first 3 hours then increased more rapidly for the next 2 hours before beginning to plateau.

Visible light absorption of virgin and hydrogenated DEB-Pd/C dispersed in a polymer matrix has not been previously reported. Previously published optical studies of DEB investigated the molecular conformation of the virgin getter without the Pd/C catalyst via ultraviolet absorption and fluorescence spectroscopy [22-25] and infrared Raman spectroscopy [26]. The colorless appearance of pure DEB and the optically clear silicone elastomer suggest that absorption of 670 nm light by the getter composite film is primarily due to the Pd/C. The decreased absorption following hydrogen exposure may be due, at least in part, to swelling of the getter composite film caused by hydrogenation of the embedded getter, effectively reducing the Pd/C concentration. The increase in vapor pressure by ~3 orders of magnitude at room temperature [27] and ~50% decrease in melting point [14] suggest a reduction of intermolecular attraction in the hydrogenated compound, possibly caused by increased spacing between molecules and resulting in volume expansion of the silicone elastomer matrix.

3.2. Sensor performance

The sensor output as a function of exposure time to 5% hydrogen in argon is shown in Fig. 6. A region of relatively low sensitivity precedes the region of maximum sensitivity (4.2 nA/h) between 6 and 13 hours of exposure. Though the response timescale is longer due to inhibition of gas flow to the getter composite film by the mirror, this trend agrees with the transmittance data shown in Fig. 5 obtained with the mirror removed. The increasing sensor signal corresponds to decreasing absorption of the laser light by the getter composite film as hydrogen is captured. The sensitivity begins to decrease again after 13 hours, indicating an optimal operating window of 7 hours at the given hydrogen concentration and flow conditions. Subsequent tests using fresh transduction films in the sensor showed similar responses under the same conditions (data not shown in figures); however, actual output values for a given exposure time differed by as much as ~20 nA for different films as a result of the non-uniform dispersion of the getter in the polymer film relative to the areas of the film sampled by the 400 μm diameter optical fibers (since the film is located at the face of the fiber bundle, the diameter of each sampled area is approximately equal to the fiber diameter). A "control" sensor constructed using a pure silicone elastomer film (no getter) showed little change during a 28 hour exposure (data not shown in figures), confirming that the change in sensor output was due to the uptake of hydrogen by the getter. The output of a "pre-conditioned" sensor during periodic hydrogen exposures is shown in Fig. 7. This sensor was pre-exposed to 5% hydrogen in argon for 6 hours prior to use, allowing it to operate at maximum sensitivity from the start. The dosimeter behavior is evident as the output increases during steady hydrogen exposure and remains constant when the exposure stops. The sharp transitions of the output when the hydrogen exposure stops and starts indicate a rapid response to the changing environment.

The sensor output was recorded as a function of gas exposure time to demonstrate the response to a steady hydrogen concentration. Because the sensor inherently monitors cumulative gas exposure, its output increased with time, whereas common hydrogen sensors would yield a constant signal in a similar environment. The sensor response is primarily governed by the uptake kinetics of the getter composite film, which are comprised of several processes: 1) diffusion of the hydrogen molecules in the film, 2) dissociation of the hydrogen molecules into atomic hydrogen by the Pd/C catalyst, and 3) bonding of the hydrogen atoms to the DEB. Various analytical methods have been used to quantify the hydrogen uptake of DEB-Pd/C and related getters, including measuring the weight change of the getter [20,27], measuring the pressure drop in a gas chamber that occurs as the getter captures hydrogen [11,21,27], and analyzing the getter composition using proton nuclear magnetic resonance spectroscopy [26]. Gas chromatography mass spectrometry has also been used to quantify the hydrogenation of DEB-Pd/C [28,29] and other unsaturated hydrocarbons [30]. The uptake rate increases with hydrogen partial pressure for DEB-Pd/C [20,21,31,32] and related getters [11,27,33]. The sensor response is therefore expected to depend on the hydrogen partial pressure (i.e., faster increase at higher partial pressure). The faster response observed when the mirror inhibiting gas flow to the getter composite film was removed suggests that the sensor output would increase more rapidly at elevated hydrogen levels.

3.3 Calibration requirements

Because proper calibration requires further device development beyond the scope of this initial study, data from calibrated sensors is not included. Calibration will be accomplished by acquiring an output signal versus exposure time curve at a constant hydrogen concentration as in Fig. 6. Such a curve will be used to convert the output signal to cumulative (time-integrated) hydrogen exposure expressed as %-hours, for example. Because the change of transmittance of the getter-polymer composite film is irreversible, calibrating the sensor by exposing it to hydrogen renders the sensor unusable. Therefore, a universal calibration curve will need to be established based on the average response of many films. At the current development stage, different films show similar behavior but the actual output values vary widely from film to film due to non-uniform loading of the getter in the film, precluding accurate calibration. This variation is evident when the curves in Fig. 6 and Fig. 7 for two different films are compared. In Fig. 6, a sensor output of 30 nA indicates an exposure of approximately 12 hours. Taking the first 6 hours as the pre-conditioning exposure step, the indicated exposure is 6 hours, or 30 %-hours. For the pre-conditioned sensor response in Fig. 7, an output of 30 nA indicates an exposure of less than 3 hours, or 15 %-hours (taking into account the removal of the sensor to air for two 30 minute periods), which is half the value indicated by the other film. In addition, the curve in Fig. 6 has a relatively long linear region compared to that in Fig. 7 whose slope gradually decreases with exposure. To provide an accurate, repeatable calibration, a refined film fabrication process must be developed to ensure acceptable uniformity among the films. Alternatively, or additionally, the sensor design may be modified to increase the area sampled by each optical fiber such that the microscopic non-uniformity is insignificant.

Once the fabrication process is refined, performing separate calibrations at various hydrogen concentrations (within a range that is relevant to the desired application) will be necessary to verify that a single calibration scale is applicable, within some acceptable degree of accuracy, to all hydrogen concentrations in the specified range. Optimally, the cumulative exposure measured by the sensor should be independent of the hydrogen concentration. In other words, for a given cumulative exposure (in %-hours) the sensor should yield the same output (in nA) whether it was exposed to a high concentration for a short time or a low concentration for a long time. Previous studies indicate that the hydrogen uptake rate of the DEB-Pd/C getter loaded in silicone elastomer varies approximately linearly with the hydrogen concentration [20,21]. Therefore, the sensor output (in nA) is expected to vary approximately linearly with the hydrogen concentration, assuming the sensor output is proportional to the uptake of hydrogen by the getter. Such a linear relationship would provide a measurement of cumulative exposure that is independent of the hydrogen concentration. The actual degree of independence must be determined experimentally.

4. Conclusion

A novel prototype optical fiber-based sensor for monitoring cumulative hydrogen exposure was demonstrated. Chemical-to-optical transduction was accomplished by measuring the 670 nm laser intensity transmitted through a transduction element comprised of the organic hydrogen getter DEB and Pd/C catalyst embedded in a silicone elastomer matrix. The transmittance of the transduction element irreversibly increased as hydrogenation of the getter progressed. The sensor exhibited a 7 hour window of maximum sensitivity following a period of initially low sensitivity when exposed to a steady flow of 5% hydrogen in argon gas at room temperature. Pre-conditioning the sensor by temporarily exposing it to hydrogen before use enabled operation at maximum sensitivity. The current prototype fabrication process yielded microscopically non-uniform loading of the getter in the polymer film, resulting in considerable variation in the sensor output for different films. Refinement of the fabrication process is necessary to fully test, calibrate, and assess the accuracy of the sensor over a range of hydrogen concentrations.

This initial study demonstrated a new means of hydrogen sensing using an organic getter-based transducer. Since its response provides an indication of cumulative exposure, the sensor may complement traditional hydrogen sensors used to provide an instantaneous reading of the hydrogen level. Further characterization of the sensor response to various hydrogen partial pressures, temperatures, and background environments (e.g., air) is needed to elucidate its utility for specific applications.

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Biographies

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His research interests include imaging, x-ray science and technology, micro-sensors, and medical devices.

Figure Captions

Fig.1. Chemical structure of a (a) completely unsaturated (virgin) and (b) fully saturated DEB molecule. Before hydrogenation, two alkyne linkages connect the three phenyl rings (molecular formula $C_{22}H_{14}$). Four hydrogen molecules catalytically dissociate into 8 hydrogen atoms that react to form the saturated molecule ($C_{22}H_{22}$).

Fig. 2. Photomicrograph of the 125 μm thick silicone elastomer film doped with 10% DEB-Pd/C by weight. Bar = 200 μm.

Fig. 3. (a) Schematic of the optical system. Light from the diode laser is directed via optical fibers to a photodiode used to monitor the laser output and to the sensor unit. Cross-sections of the fiber bundles leading to the sensor unit and the photodiode providing the sensor output are illustrated. (b) Exploded view and (c) photograph of the prototype sensor unit. Four gas flow channels in the housing fixture surround the components to allow hydrogen exposure of the getter composite film. The overall diameter of the housing fixture is 9.5 mm.

Fig. 4. Schematic of the gas flow system used to expose the sensor to a steady flow of 5% hydrogen in argon at room temperature. The Ultra-Torr union used to prevent leakage between the fiber bundle ferrule and the sensor housing is indicated by a dotted outline for clarity. The premixed gases are introduced from a gas cylinder (not shown) and are bubbled through mineral oil (not shown) to exit the system.

Fig. 5. 670 nm transmittance of the DEB-Pd/C composite film as a function of exposure time to 5% hydrogen in argon at room temperature.

Fig. 6. Sensor output over the course of a steady exposure to 5% hydrogen in argon at room temperature. The output is nearly linear (4.2 nA/h) in the region of highest sensitivity between the 6 and 13 hour time points.

Fig. 7. Response of a pre-conditioned sensor to intermittent 5% hydrogen in argon exposure. The sensor was periodically removed from the flow system to the ambient air for 30 minute intervals.

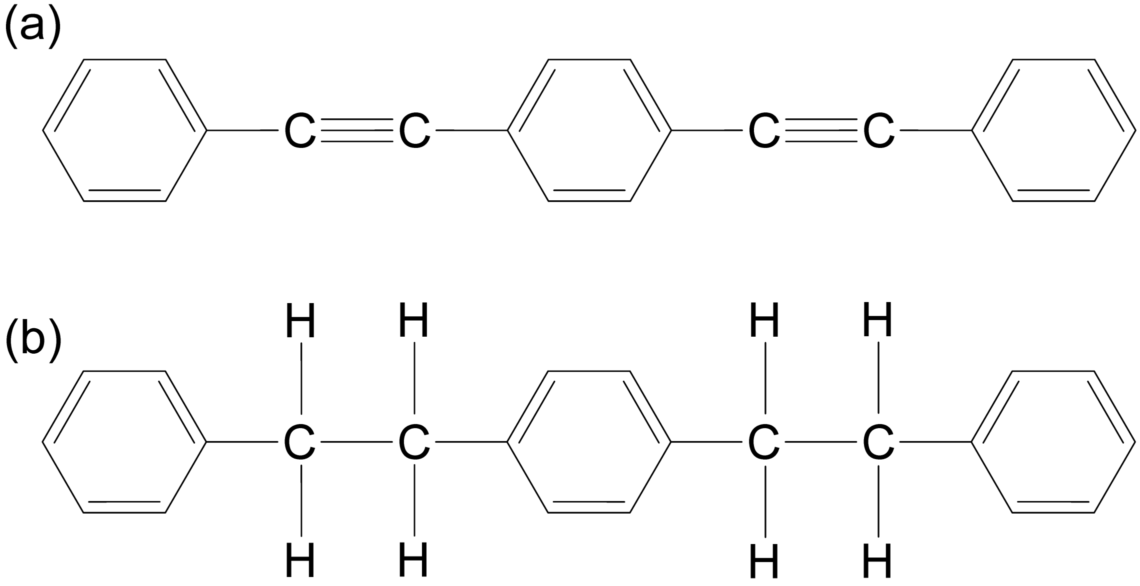

Fig. 1

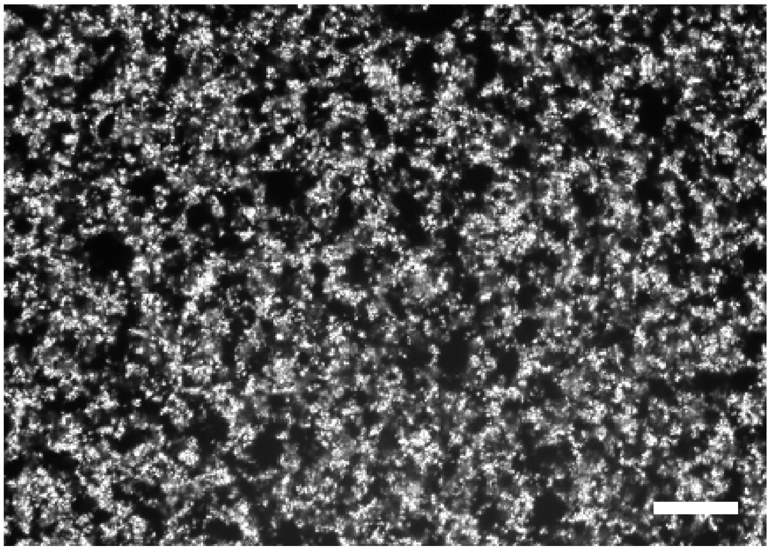

Fig. 2

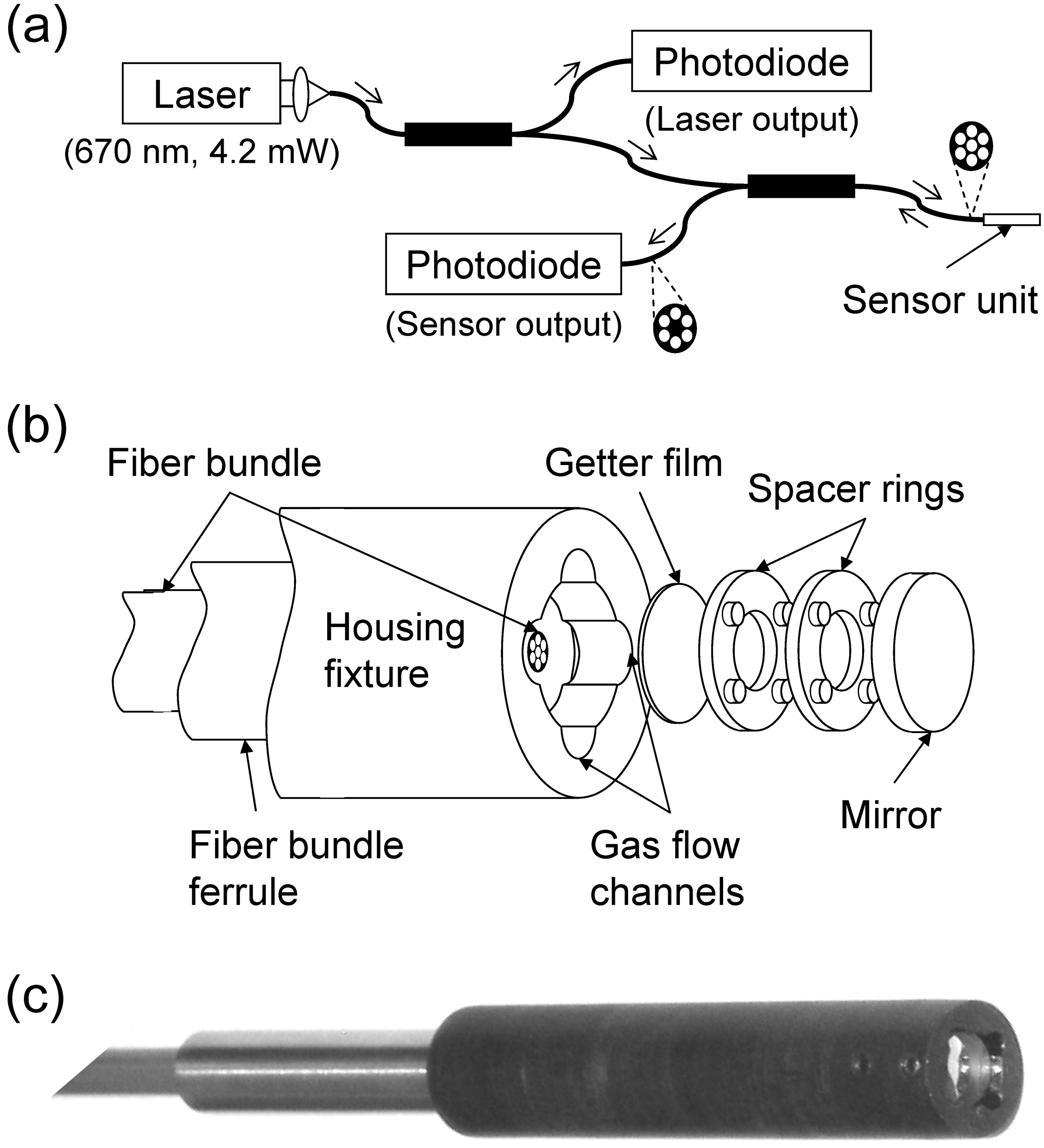
(a)
Laser
(670 nm, 4.2 mW)
Photodiode
(Laser output)
Photodiode
(Sensor output)
Sensor unit
(b)
Fiber bundle
Getter film
Spacer rings
Housing fixture
Mirror
Fiber bundle ferrule
Gas flow channels
(c)

Fig. 3

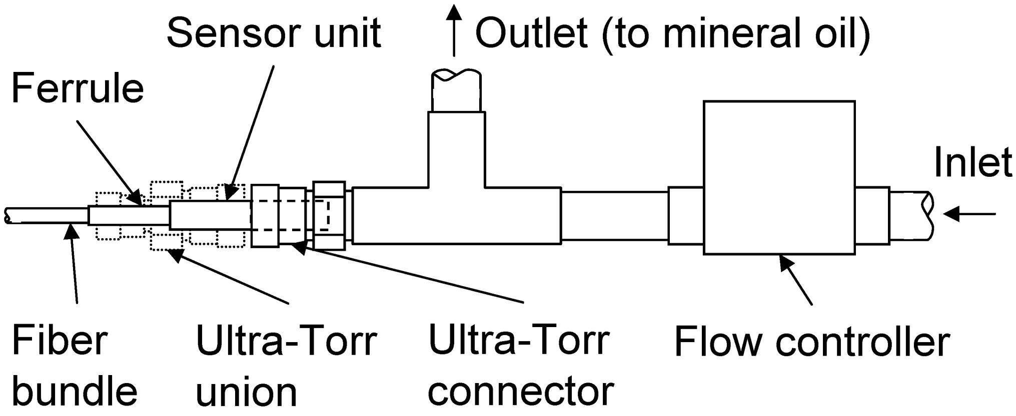
Sensor unit
Outlet (to mineral oil)
Ferrule
Inlet
Fiber bundle
Ultra-Torr union
Ultra-Torr connector
Flow controller

Fig. 4

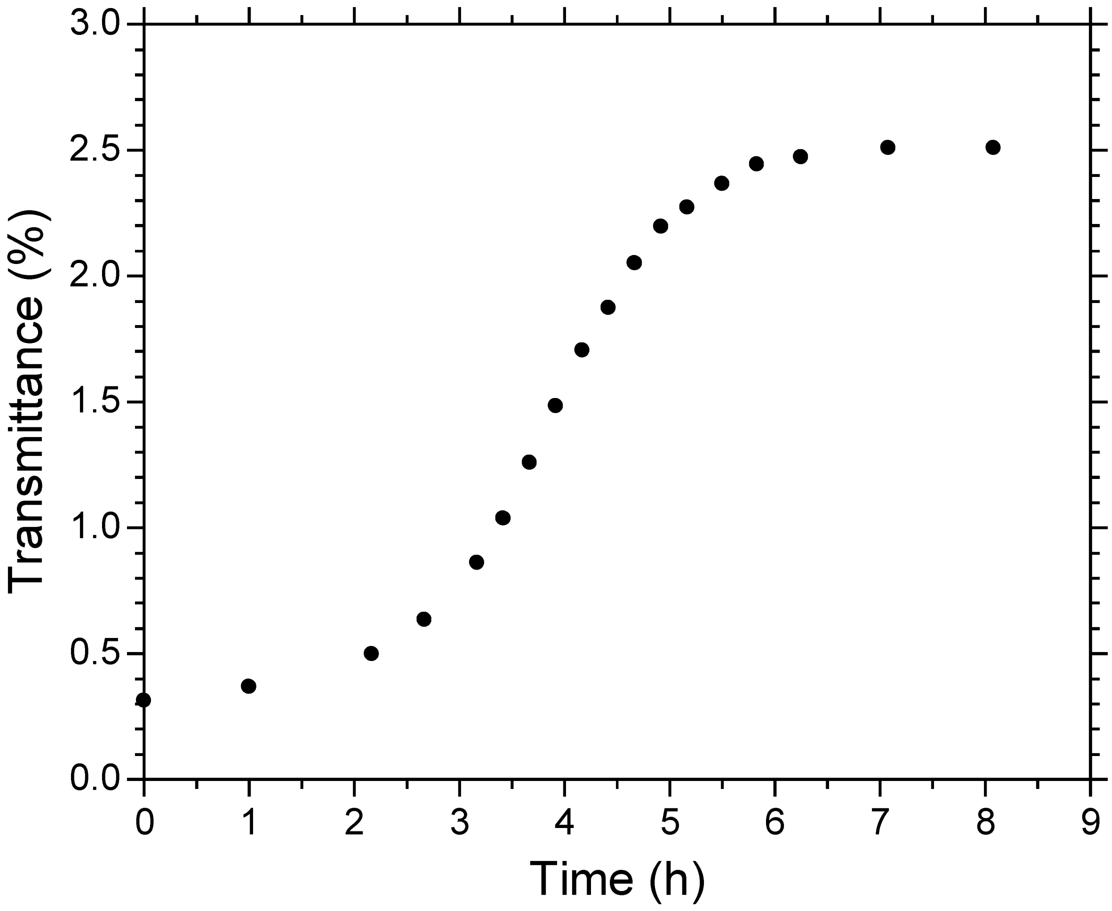

Fig. 5

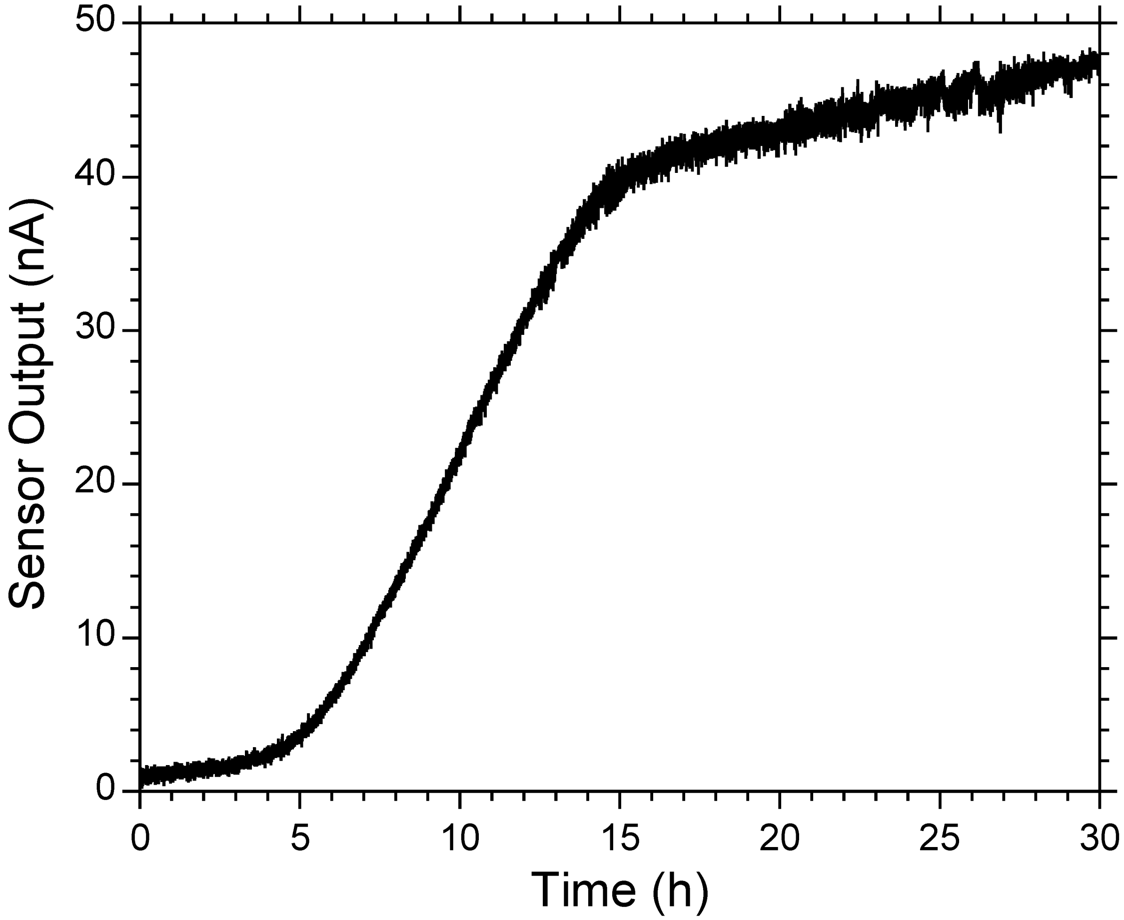

Fig. 6

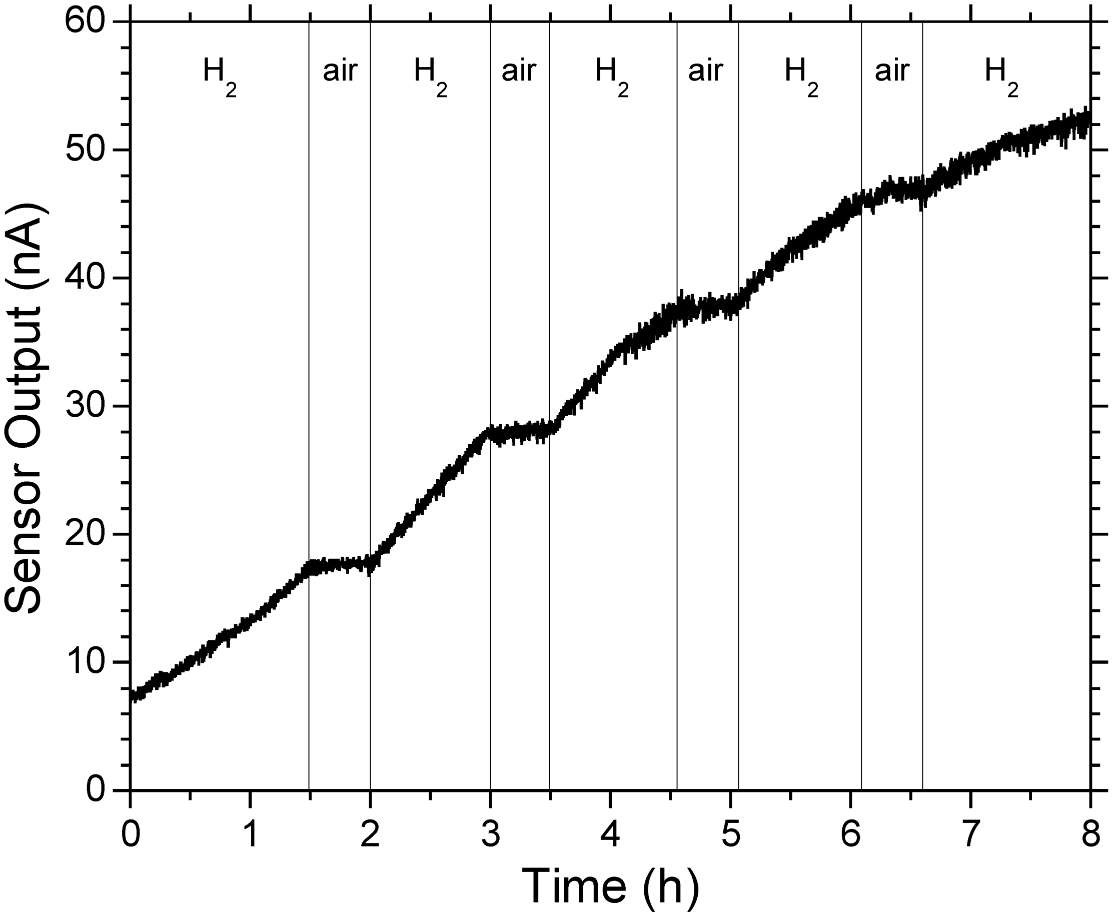
Sensor Output (nA)
Time (h)
0
10
20
30
40
50
60
0
1
2
3
4
5
6
7
8
H_2
air
H_2
air
H_2
air
H_2
air
H_2

Fig. 7