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A fiber optic sensor with a metal organic framework as a sensing material for trace levels of water in industrial gases

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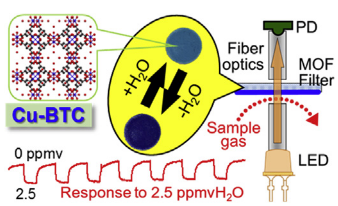
HIGHLIGHTS

- The color changes of Cu-BTC with trace water was investigated.
- A fiber optic gas sensor with metal organic frameworks as sensing material was well designed with solid state devices.
- Relatively rapid and sensitive sensor for trace water in industrial gases were developed.
- No significant effects on the sensitivity was observed by sample flow rate, and various kinds of sample gases.

GRAPHICAL ABSTRACT



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ABSTRACT

Industrial gases such as nitrogen, oxygen, argon, and helium are easily contaminated with water during production, transfer and use, because there is a high volume fraction of water in the atmosphere (approximately 1.2% estimated with the average annual atmospheric temperature and relative humidity). Even trace water (<1 parts per million by volume (ppmv) of H_2O, dew point < −76 °C) in the industrial gases can cause quality problems in the process such as production of semiconductors. Therefore, it is important to monitor and to control trace water levels in industrial gases at each supplying step, and especially during their use. In the present study, a fiber optic gas sensor was investigated for monitoring trace water levels in industrial gases. The sensor consists of a film containing a metal organic framework (MOF). MOFs are made of metals coordinated to organic ligands, and have mesoscale pores that adsorb gas molecules. When the MOF, copper benzene-1,3,5-tricarboxylate (Cu-BTC), was used as a sensing material, we investigated the color of Cu-BTC with water adsorption changed both in depth and tone. Cu-BTC crystals appeared deep blue in dry gases, and then changed to light blue in wet gases. An optical gas sensor with the Cu-BTC film was developed using a light emitting diode as the light source and a photodiode as the light intensity detector. The sensor showed a reversible response to trace water, did not require heating to remove the adsorbed water molecules. The sample gas flow rate did not affect the sensitivity. The obtained limit of detection was 40 parts per billion by volume (ppbv). The response time for sample gas containing 2.5 ppmvH_2O was 23 s. The standard deviation obtained for daily analysis of 1.0 ppmvH_2O standard gas over 20 days was 9%. Furthermore, the type of industrial gas did not affect the sensitivity. These properties mean the sensor will be applicable to trace water detection in various industrial gases.

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1. Introduction

Metal organic frameworks (MOF) are mesoporous structures consisting of metal ions or clusters coordinated to organic ligands [1]. A well-known MOF is Prussian blue, which contains Fe(II), Fe(III), and CN^- and has a porous three-dimensional structure which is effective to adsorption of gas molecules or ions. Recently, Prussian blue has been studied for the selective adsorption of radioactive Cs^+ from contaminated water [2] and the human body [3]. MOFs typically have high gas adsorption efficiencies because of their varied pore sizes [4]. MOFs are of interest in the areas of energy storage (adsorption of H_2 and CH_4) and removal of CO_2 to decrease greenhouse effects [1] as strong adsorbent.

In analytical chemistry, MOFs have been used to adsorb gases [5,6], and to separate materials in gas chromatography [7] and liquid chromatography [8]. MOFs have also been used in chemical sensors to adsorb gases [9], which are then detected using a quartz crystal microbalance [10] or surface plasmon resonance [11] to monitor changes in the weight of the MOF. MOFs can show chromism and change color in response to adsorption of solvents or vapors [9]. However, to date, no practical sensors with MOFs with sufficient sensitivity, selectivity, and chromism have been reported.

Fiber optic gas sensors were prepared in earlier studies by one of the authors. These sensors were based on solid phases impregnated with reagents to collect and concentrate the analyte, and show color changes in response to the analyte for detection. Atmospheric NO_2 and O_3 have been detected simultaneously with the reagent 8-aminonaphthylsulfonate, which reacts with NO_2 and O_3 to generate different colors [12]. In this case, light emitting diodes (LEDs) and a photodiode (PD) were used to observe the developed colors, and atmospheric NO_2 and O_3 were detected within 5 min [12]. A fiber optic gas sensor with calix[4]arene derivatives has been used to detect reversibly parts per million by volume (ppmv) levels of NO_2 [13], and a sensor with cobinamide has been used to detect cyanide in blood after pervaporation by the colored vitamin B12 [14]. These studies support applicability of MOFs that show chromism as fiber optic gas sensors.

In the present study, fiber optic gas sensors with MOFs for trace water was developed for the analysis of high-purity industrial gases, which are used in instrumental analyses, semiconductor, and chemical industries. Industrial gases such as N_2, He, Ar, and O_2 are produced cryogenic distillation of air. Trace water is a common contaminant from atmosphere, and it is difficult to remove completely. Furthermore, the water molecules are easy to adsorb on the surfaces of pipes and tanks then released into the purified gases. Atmospheric water, which is present at a volume fraction of 1.2% estimated with average annual temperature (17.1 °C) and humidity (62%RH) in Tokyo, Japan on 2014, can contaminate pure gases. Trace water in purified gases can generate problems at use point such as ghost peaks in gas chromatography, and defect in semiconductor products like loss of light emitting efficiency in LEDs [15]. The effect of few ppmv of trace water in hydrogen environment on the tribological effects has also been detailed [16]. Quality control analysis of gases used in an industry is important at each stage, including production, transfer, and use of the gas. The required levels of trace water in purified gases have decreased with integration and downsizing in semiconductor productions. In 2007, the National Metrology Institute of Japan established a certified reference material for trace moisture in nitrogen using a permeation tube method [17]. Since 2009, this method has been used to provide traceability to National Institute of Standards and Technology (NIST) for trace water at levels from 12 to 1200 nmol mol^{-1}. There are only a few analytical instruments that can be used for trace water detection [18], including chilled mirror hygrometers [19], thin alumina film capacitive sensors [20], amperometric P_2O_5 film sensor [21], Fourier transform-infrared spectrometers [22], atmospheric pressure ionization mass spectrometers [23], and cavity ring down spectrometers (CRDS) [24,25]. These instruments are commercially available and perform well [26,27]. However, some issues remain with these methods. For example, while CRDS functions well with good responses and stability for measurement of trace water, it requires a high-quality pulsed laser light source and an optical system, which are expensive to setup for continuous monitoring at each stage (production, transfer, and use). Furthermore, the sensitivity of CRDS is affected by the type of bulk gas to be analyzed. Chilled mirror hygrometers possess accuracy problems for trace water monitoring, and some alumina film capacitive sensors have a difficulty on the detection trace water or have a long response time (approximately 8 h) [26,28].

In the present study, a fiber optic gas sensor containing a MOF as sensing material was developed for ultra-trace levels of water in high-purity industrial gases.

2. Experimental methods

2.1. Fiber optic gas sensor set-up

The set up of fiber optic gas sensor is shown in Fig. 1. The sensing material, Basolite®C 300 (copper benzene-1,3,5-tricarboxylate, Cu-BTC) was obtained from www.sigmaaldrich.com. A MOF filter for gas collection was prepared by suspending Cu-BTC (3.0 mg) in 15 mL of acetone. An aliquot of the fully-mixed suspension (5.0 mL) was passed through a polytetrafluoroethylene filter (ø 10 mm, thickness 0.54 mm, PF020, www.advantec.co.jp) in a Swinnex® filter holder (SX0001300, www.emdmillipore.com). The filter was dried under a stream of pure nitrogen gas for 1 h, and then stored in a desiccator.

The prepared filter was placed in a gas collector/absorbance detector. The sample gas was blown onto the filter surface through a stainless steel tube (AWG 13G, ø 1.99 mm inner diameter, ø

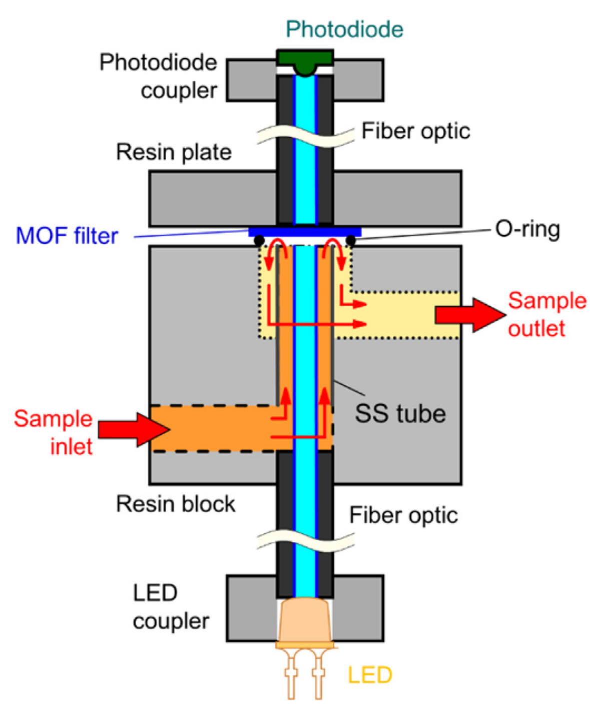

Fig. 1. Schematic of the fiber optic gas sensing device.