Results in Physics 7 (2017) 323–326

Contents lists available at ScienceDirect

Results in Physics

journal homepage: www.journals.elsevier.com/results-in-physics

Optical carbon dioxide sensor based on fluorescent capillary array

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ARTICLE INFO

Article history:
Received 5 December 2016
Received in revised form 24 December 2016
Accepted 26 December 2016
Available online 29 December 2016

Keywords:
Carbon dioxide chemical sensor
Fluorescence sensor
Capillary array

ABSTRACT

A novel carbon dioxide (CO_2) gas sensor based on capillary array is presented. The capillary array is composed of 51 capillaries and modified by fluorescent dye 8-hydroxy-1,3,6-pyrenetrisulfonic acid trisodium salt (HPTS, PTS^-) and tetraoctylammonium cation (TOA^+) doped porous ethyl cellulose. A Y-fiber is used to transmit exciting light and fluorescence. A fiber optic pigtail-contained spectrophotometer is used to collect and deal with optical signals. Due to its structural features, each capillary has the two rolling-up layers of inner and outer sensing films, which make the 2 cm long capillary array has large sensing area about 12.81 cm^2 and the fluorescence signal easily be collected. The sensing probe has advantages such as small volume, compact structure and large sensing area. The results demonstrate that the sensor has a linear response in the CO_2 volume ratio range from 0 to 10%.

Introduction

The measurement of carbon dioxide level in the atmosphere and other gases is of fundamental importance in a wide variety of applications such as chemical and clinical analysis, environmental air quality [1–7]. For humans, in enclosed spaces such as mines, wells and sewers, a gas mixture containing 5–20% CO_2 is required by safety regulations [8]. The increase of the carbon dioxide concentration in atmosphere, one of the three major atmospheric contributors to the greenhouse effect, which further showed the importance of measuring the concentration of carbon dioxide. The CO_2 sensors are mainly based on infrared (IR) absorptiometry, electrochemical sensor device and optical techniques. The infrared absorptiometry based CO_2 sensor is subject to strong interference from water vapor, and the sensor is relative expensive [9,10]. CO_2 optical sensors based on fluorescence intensity or absorption changes of indicators have been extensively studied. They have several advantages such as reduced noise interference, electrical isolation and possible miniaturization. The fluorescent reagent HPTS has been employed in many CO_2 optical sensors due to its distinct absorption/emission bands in visible light region. Based on the HPTS, researches have present a reservoir type of capillary CO_2 microsensor and another novel CO_2 sensors which used emulsion of room-temperature ionic liquids in a silicone matrix. The second CO_2 sensors exhibit excellent linearity of the calibration plots and good long-term stability [11]. Aller et al. developed a fluorescent sensor with high resolution two-dimensional imaging of pCO_2 distributions in sediments and overlying water by using HPTS [12]. However, all the sensing films are planar films which cause relatively difficult to collect the optical signals. In order to resolve this problem, we developed a novel CO_2 sensor by employing capillary array.

In this paper, we present the fabrication of a CO_2 gas sensor based on an array with 51 glass capillaries. The channels of the capillaries and the gaps between capillaries are modified by CO_2 sensitive films. In measurement of CO_2 gas, the channels and gaps are used not only for gas flowing, but also for gas sensing. Meanwhile, as optical waveguide media, the capillaries array is responsible for transmitting optical signals. This sensor adopts low cost material but has large sensing area and compact structure. The sensing performance is studied in this paper.

Experimental

Sensor composition

As shown in Fig. 1, the sensor used for measuring CO_2 concentration is composed of a 450 nm laser diode (LD) as the light source, 2 cm length of CO_2 sensitive capillary array with outer diameter about 3 mm, an auto-suctioning device, a Y-fiber and a fiber optic pigtail-contained spectrophotometer. All component parts are connected by elaborate moulds and the joints are sealed by a black thermosetting tube to avoid external light interference.

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http://dx.doi.org/10.1016/j.rinp.2016.12.044
2211-3797/

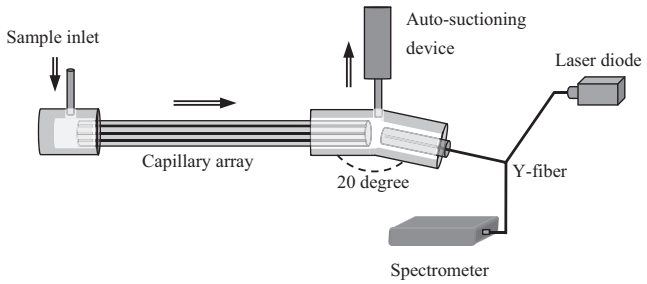

Fig. 1. The schematic structure of the carbon dioxide gas sensor.

The capillary array adopted here is composed of 51 capillaries made of glass. The hole diameter of every capillary is about 100 μm. The channels of the capillaries and the gaps between capillaries are modified by CO_2 sensitive films. In experiment, the exciting light coming from the LD passed though the Y-fiber and transmits into the glass substrate of capillaries and then excites the fluorescence of rolling-up sensing films. The resulting fluorescence directly or after scattering or passing though the glass capillaries transmits into Y-fiber and finally collected by the spectrophotometer. There is an angle about 20 degree between the glass capillaries array and the Y-fiber. Though this angle reduces the exciting light power into the glass capillaries array, this design could effectively reduce the reflected exciting light which easily cause light saturation of the spectrophotometer. The design makes the most of reflected exciting light does not enter the optical fiber and spectrophotometer, so the spectrophotometer could normally measure the fluorescence. The sensor has an auto-suctioning device to inhale the gases. In the experiment, the air thoroughly passed through the inlet, the sensing film modified capillary array and the auto-suctioning device.

Preparation of the sensing array

The CO_2 sensing film was prepared by the use of ion pairs consisting of the pH indicator anion PTS^- coming from HPTS and an organic quaternary cation TOA^+ coming from tetraoctylammonium bromide (TOA^+Br^-). Ethyl cellulose was used as the film-forming materials. Tetraoctylammonium hydroxide (TOAOH) was used as phase-transfer agent [11,12]. The following is the detailed procedure for preparing the sensing film. The TOAOH was prepared by stirring 0.7 g of silver oxide and 0.93 g of tetraoctylammonium bromide in 6.6 ml of ethanol for 6 h. The resulting TOAOH was centrifugated, then decanted and stored in a refrigerator. Before using, the TOAOH solution was equilibrated with 5% CO_2 in N_2 in order to form a lipophilic hydrogen carbonate buffer. $(TOA^+)_4PTS^{4-}$ ion pair was prepared as follows: 200 mg of HPTS was added to 50 mL of a 0.01 mol/L aqueous NaOH solution. To this solution 35 mL of methylene chloride containing 850 mg TOABr were added. The two phase mixture was shaken for 1 h at room temperature. The ion pair was formed and presented in the organic phase which assumed a strong fluorescence. The organic phase was separated and washed twice with 50 ml of 0.01 mol/L NaOH. The solvent was removed under vacuum and the residue dried in a desiccator to obtain $(TOA^+)_4PTS^{4-}$. A solution of 0.29 g/ml of $(TOA^+)_4PTS^{4-}$ in toluene was prepared for further use. The sensing cocktail was prepared by adding 1.25 mL of TOAOH to 1 mL of 0.29 g/ml $(TOA^+)_4PTS^{4-}$ solution. Then this solution mixed with 6 mL of a 6% ethyl cellulose solution in ethanol/toluene (10/90, v/v). This mixed solution was used for preparing sensing film.

Results and discussion

As shown in Fig. 2(a), the capillary array is fabricated by molding 51 capillaries in a transparent thermosetting tube. The capillaries are ordered in the tube. The above-mentioned mixed solution was inhaled into the channels of the capillaries under the pressure about 0.06 MPa. The mixed solution immediately spread along the inner channels of the capillaries and the gaps between capillaries. The sensing films containing ion pair was formed on the wall of channels and gaps of the capillaries after removal of the solvent molecules by inhaling air into the capillaries for several minutes. As shown in Fig. 2(b), a picture of the capillary array with sensing film was captured by a microscope when it was excited by a light source of 450 nm. From the picture, green fluorescence could be clearly seen. It demonstrates that the sensing film was formed in the capillary array.

The optical and chemical mechanism involved in the gas sensor is described in Fig. 3. The basic (dissociated, PTS^-, exists as TOA^+-PTS^-) forms of HPTS has an absorption peak of 467 nm in visible range. According to Fig. 3, an LD with the emission wavelength of 450 nm is chosen as the exciting light source. In experiment, the basic (dissociated, PTS^-) forms of HPTS exhibits the fluorescence with the emission maximum at 523 nm when it is excited by the light of 450 nm wavelength from LD. However, the acidic (associated, HPTS) forms of HPTS has no fluorescence when it is excited by the same LD. This phenomenon provides the possibility for measuring the concentration of CO_2. As shown in Fig. 4, the fluorescence of ion pair TOA^+PTS^- varies with different ratio of CO_2 gas. The principle of the fluorescence changes is as follows: as shown in Eq. (1), the TOA^+PTS^- exists as basic (dissociated, PTS^-) forms in the sensing film when it is in the gas with no CO_2. Therefore, the sensing film emits intense green fluorescence (523 nm) when it is excited by the LD of 450 nm wavelength. With the increase of CO_2 concentration, the TOA^+PTS^- is protonated and gradually loses its green fluorescence. Hence, the concentration of CO_2 in mixed gases can be measured through recording changes of the fluorescence intensity at 523 nm by the spectrometer. N_2 is used as diluent gas in N_2-CO_2 mixture.

$$CO_2\,(g) + TOA^+\,PTS^-{\cdot}xH_2O \rightleftharpoons TOA^+\,HCO_3^-{\cdot}(x\text{-}1)H_2O + HPTS \quad (1)$$

(base color) (acid color)

As shown in Eq. (1), water is essential to the reaction. The sensing film is hydrophobic because it is made of hydrophobic material of ethyl cellulose which is easily infiltrated by nonpolar CO_2. Therefore, there are no pure polar water molecules in the sensing film. The water molecules are induced into hydrophilic sites presented in the ion pair when the ion pairs mix with the phase-transfer agent TOAOH.

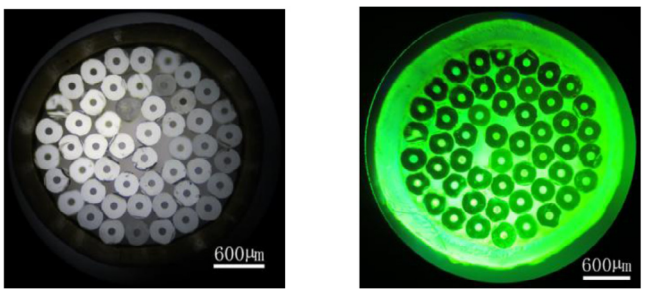

Fig. 2. Microscope pictures, (a) capillary array end-face with on sensing film, (b) capillary array with sensing film excited by a light source of 450 nm.