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Exploitation of thermo-effect of rhodamine B entrapped in sol–gel matrix and silica gel for temperature detection

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Abstract

In the present work, optical temperature sensors were prepared using a fluorescent dye, rhodamine B and different adsorbents, viz. silica gel and sol–gel. Silica gel (28–200 mesh) and a sol–gel consisting of a mixture of 3-amino-propyl-trimethoxy-silane (APTMS) and 3-glycidoxypropyl-tri-methoxy-silane (GPTMS) were used as the support matrices for the fluorescent dye. The polymerization of alkoxide silanes to produce a clear single phase sol–gel polymer at low temperature allows for the encapsulation of the fluorescence dye, and the rigidity of the silica gel prevents the movement and interaction of intermolecules, while still allowing them to retain their activity. The linear detection ranges of the fiber optic temperature sensors (FOTS) were between 10–95 °C and 0–60 °C when using silica gel and sol–gel as the support materials, respectively. The planar optic temperature sensors (POTS) showed high sensitivity in the temperature range of 25–40 °C. The interferences and life-time of the temperature sensors were also investigated.

Keywords: Temperature; Sensor; Sol–gel; Silica gel; Fiber optic; Fluorescence

1. Introduction

Temperature is an essential physical parameter in all fields of science and process control technology [1]. Among the many types of temperature sensors, various optical temperature sensors have been designed and manufactured using optical fibers or optical waveguides. These optical fiber sensors usually showed many advantages over their electrical counterparts, such as high sensitivity, small size, safety in hazardous or explosive environments and the potential for signal processing over large distances [2].

The optical temperature sensors developed so far used a number of different sensing methods such as absorption [3], fluorescence [4–5], Raman [6], Bragg grating [7], interferometry and other spectroscopic techniques [8]. A number of optical temperature sensors have been developed based on fluorescence techniques, e.g. the fluorescence life-time, amplified spontaneous emission or fluorescence intensity, etc. The fluorescence method is one of the most sensitive ones, because the excitation and emission of light can be separated resulting in low background noise. Optical temperature sensors based on the fluorescence technique can also cover a relatively wide sensing range with reasonable resolution [9–10].

In order to fabricate a fluorescence-based temperature sensor, fluorescence materials which have a sufficiently strong dependence on temperature need to be used as the sensing element. Some ions of rare earth elements such as erbium, activated or doped in optical fibers, have been extensively used to develop optical temperature sensors [11–12]. Even though rare earth doped optical temperature sensors are applicable over a wide temperature range, e.g. −50 to 600 °C [13], the fabrication of sensor probes, i.e. the doping of rare earth elements, is somewhat complex. Therefore, a simple and reliable method of immobilizing fluorescence dyes is required for the development of optical temperature sensors.

Recently, an oxygen sensitive dye like $Ru(bpy)_3^{2+}$ was used for temperature sensing after its encapsulation into poly(vinyl alcohol) (PVA) films [14]. Some fluorescent dyes such as tetraphenylporphyrin (TPP) have been also immobilized onto the tip or side of an optical fiber for the measurement of O_2, pH and

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CO_2 by the sol–gel techniques [15–16]. The sol–gel technique has several advantages over other immobilization techniques used for dye molecules. Apart from its simplicity, the encapsulation of dyes into sol–gels makes the sensor more practical and resistant than other methods in aggressive environments or biological systems.

In this work, optical temperature sensors were fabricated based on the quenching of the fluorescence of a dye, rhodamine B. As in theories, rhodamine B was well known as a sensitive temperature indicator. It was added to liquid flow [17] or attached on the surface of glass beads [18] to measure temperature based on the change in fluorescence intensity. However, these sensing systems showed their ability only in the detection range of 20–80 °C and could not recover the fluorescence intensity at high temperature due to limited capability of supporting material [18]. Therefore, in our sensing models rhodamine B was incorporated into a silica gel or sol–gel matrix since those are proved as useful supporting materials in many fields [19–20]. The rhodamine B entrapped into a silica gel or sol–gel based solid matrix is coated onto the tip of an optical fiber probe (fiber optic temperature sensor (FOTS)) or onto the surface of a well in a 96-well microtiter plate (planar optic temperature sensor (POTS)) and then they enabled to measure the temperature of aqueous solution. The design of these sensing models originate from the requirements of temperature sensing in fermentation processes, especially for testing cultivation conditions of microorganisms on microtiter plates since it needs small sample volume and simultaneous screening of high numbers of samples. Other characteristics of these sensing systems, such as their interferences and stability, were also investigated.

2. Experimental

2.1. Materials

Rhodamine B, silica gel 28–200 mesh, 3-glycidoxypropyl-tri-methoxy-silane (GPTMS) and 3-amino-propyl-trimethoxy-silane (APTMS) were purchased from Sigma Chemical Company (Seoul, Korea). All other chemicals were of analytical grade and used without further purification.

2.2. Preparation of the optical temperature sensors

2.2.1. Fiber optic temperature sensor (FOTS)

For the fabrication of the fiber optic temperature sensor, two kinds of support matrix were used for the fluorescent dye, viz. silica gel and a sol–gel. The dye adsorption of the silica gel was performed in 0.1 mM rhodamine B solution. The dye adsorbed silica gel was washed with ethanol until the waste solution had a light pink color and then dried at 60 °C for several hours. The dried and adsorbed silica gel was attached to the end of the fiber using transparent silicon (Elastosil-E43, Wacker-Chemie GmbH, Munich, Germany). Following this, the sensor was kept at room temperature for 10 h and then covered in a thin black silicon layer (Elastosil-E43, Wacker-Chemie GmbH). After storing it for 2 h at room temperature, the sensor was ready for measurement.

The sol–gel solution was prepared by mixing APTMS, GPTMS and 99% ethanol at a ratio of 25:6.25 (vol. %). 0.1 mM rhodamine B solution was added to the sol–gel at a volume ratio of 10% and aged for about 2 h under shaking conditions. The end of the fiber was dipped in this mixture, then taken out and kept at room temperature for 10 h. The subsequent steps were the same as those used in the preparation of the fiber optic temperature sensor using silica gel.

2.2.2. Planar optic temperature sensor (POTS)

In this case, only sol–gel was used as the support matrix for the fluorescent dye. The procedure used for the preparation of the sol–gel solution is similar to that described in Section 2.2.1. After the sol–gel was prepared, 1 μM rhodamine B solution was added to the sol–gel at a volume ratio of 7.4%. The mixture was stirred at 37 °C for half an hour and then deposited on the bottom of the wells of a 96 well microtiter plate (Nunc Co., Roskilde, Denmark). The microtiter plate was heated in an oven at 60 °C for 24 h prior to use.

2.3. Measurements of fluorescence intensity

The fiber optic temperature sensor was connected to an optical measurement instrument (MOPS04, Comte GmbH, Hannover, Germany). The change in temperature of the samples was correlated with the change in the fluorescence intensity. The yield of the fluorescence intensity was converted to voltage units. The sensor was dipped in a water circulating bath equipped with a temperature controller (JeioTech Co., Seoul, Korea). The influence of pH on the fiber optic temperature sensor was evaluated in carbonate buffered pH solutions. The influence of the ionic strength was investigated in 10 mM sodium phosphate buffer solutions (pH 7.0), to which adequate amounts of sodium chloride were added in order to vary the ionic strength in the range of 10–500 mM.

For the measurement of the planar temperature sensor, the fluorescence intensity was measured from the bottom of the microtiter plate using a microplate reader (Wallac Victor 2, Perkin-Elmer Co., Wellesley, MA, USA). Bandpass filters of 485 and 535 nm were used for emission and excitation, respectively. The plate reader was equipped with an incubator with a temperature range of 15–45 °C; however, the temperature range used in this study was of 25–40 °C. Before the measurement, the sensing membrane in the wells was covered with a thin layer of transparent silicon (Elastosil-E43). The fluorescence of rhodamine B was identified using a fluorescence spectrophotometer (F-4500, Hitachi Co., Tokyo, Japan) and a microplate reader.

2.4. Data analysis

Measurement data are presented as mean ± S.D. (standard deviation). The differences in the fluorescence intensity at different pH values and ionic strengths were assessed by one-way analysis of variance (ANOVA). The differences observed