



Microfluidic optoelectronic sensor based on a composite halochromic material for dissolved carbon dioxide detection



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ABSTRACT

We present a microfluidic optoelectronic cross-reactive sensor based on a novel composite material for selective detection of dissolved CO₂. A microfluidic device contains an array of micro-wells filled with ion-exchange polymeric microbeads doped by halochromic dyes paired to quaternary ammonium cations. The sensor configuration allows incorporation of virtually any combination of halochromic ion-pairs, providing a route for cross reactive sensing. A versatile optical arrangement based on a white LED and a miniature portable USB spectrometer allows recording optical spectra, which are easily translated into electronic readouts. Rather than monitoring response at a particular absorption or emission wavelength of the dye, data acquisition is performed over a broad continuous spectrum. This results in a rich multidimensional readout useful for ultrasensitive detection. The sensor provides distinctive responses to different concentrations of dissolved CO₂, with no cross sensitivity to other sources of acidity. Our findings could lead to the development of a cost-effective, lightweight, and low-power sensor for detection of dissolved CO₂ for a variety of applications.

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1. Introduction

Detection of carbon dioxide (CO₂) is of great importance in a variety of fields, including life sciences, medicine, biotechnology, environment and agriculture. Conventionally, CO₂ detection was based on either IR absorption measurement (4200–4400 nm) or electrochemical measurement using Severinghaus electrode [1,2]. While IR spectroscopy provides quick response times and high accuracy, it is bulky and expensive. In addition, due to its inherent disadvantage of strong interference by water vapor, IR spectroscopy is only suitable for gas phase. The Severinghaus type CO₂ electrode comprises of a pH electrode immersed in a bicarbonate buffer solution with the whole device encapsulated by a proton impermeable, but CO₂ permeable membrane. Gaseous or dissolved CO₂ diffuses through the gas-permeable membrane and equilibrates with the internal aqueous bicarbonate layer thereby altering its pH. Although widely used for dissolved CO₂ detection, the Severinghaus electrode has a number of disadvantages. Due to the introduction of a gas-permeable membrane such as Teflon and Silastic, the CO₂ electrode has relatively long response time. It also suffers from the inherent drawbacks of the pH electrode and cannot be readily miniaturized (e.g. for in vivo biological studies) [3]. Other techniques for CO₂ detection, such as gas chromatography

(GS) and mass spectrometry (MS), can provide high accuracy, but requires bulky, complex and expensive equipment.

As an alternative, optical CO₂ sensors based on *halochromic dyes* (i.e. dyes that change color as a function of pH) have been suggested for detection of both gaseous and dissolved CO₂ (either calorimetrically or using fluorescence) [1,4–10]. One possibility is to implement design, which is similar to the Severinghaus electrode, while replacing the pH electrode with a pH sensitive dye. However, the bicarbonate buffer and the CO₂-permeable polymeric membrane are still required in this configuration, resulting in a gradual drift and long response times [8]. Such sensors are also sensitive to environmental fluctuations, while maintaining the integrity of the buffer solution is a challenge.

A relatively recent approach is based on the use of an *ion-pairing agent*, a quaternary ammonium hydroxide [3,11–18]. The ion pair is formed between the quaternary ammonium cation, which can be easily incorporated into a polymeric matrix, and the pH indicator dye anion, incorporating the dye into the sensing matrix. In addition, a small amount of water of solvation is associated with the ion pair, providing water molecules necessary for sensing mechanism [3]. Importantly, the ion pair formation deprotonates the dye, serving as a buffer. Therefore, this method eliminates the need of the bicarbonate buffer. The sensing mechanism can be described in terms of the following equation [19]:



where Q⁺ is the quaternary ammonium cation, D⁻ is the deprotonated halochromic dye (HD stands for the protonated dye), and *x* is

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the number of molecules of the water of solvation. Reaction of dissolved CO₂ with the water of solvation forms carbonic acid, which forms quaternary ammonium bicarbonate and causes protonation of the halochromic dye, changing its optical properties, which can be detected calorimetrically or by fluorescence measurement. The use of halochromic dyes such as cresol red [11], pyranine [19–23], and bromothymol blue [24] has been reported, for CO₂ detection in both gas phase [11,19,24] and aqueous medium [1,11,20]. However, CO₂ detection in aqueous samples still requires some kind of hydrophobic coating, such as ethylcellulose or silicone rubber, in order to prevent the interference with background acidity whose source is not related to dissolved CO₂ [11].

Even while using organic dye/quaternary ammonium ion pair, CO₂ detection in aqueous samples with complex chemistry (e.g. bioreactors or biological fluids) is expected to be very challenging, due to undesirable processes such as leaching of sensing material and countless possibilities of interference with other chemical compounds. To overcome these drawbacks, we suggest a novel versatile sensing platform based on a new class of composite sensing material, namely ion-exchange polymer microbeads impregnated with halochromic ion-pairs, and a cross-reactive approach. As a sensing strategy, the use of cross-reactive sensors can be very efficient in analysis of complex mixtures [25–27].

We demonstrate that the unique configuration of the halochromic dye/quaternary ammonium ion pair immobilized in polymeric microbeads through ionic interactions provides excellent selectivity to dissolved CO₂, as well as distinctive sensitivity to different concentration without using any additional hydrophobic coating. A simple configuration of the PDMS microfluidic device, where polymeric microbeads with incorporated sensing material are easily entrapped within the array of microwells, is robust and inexpensive. A miniature optical setup based on a white LED and a portable USB spectrometer can read the entire optical spectrum in less than a second (instead of conventional monitoring of only a particular absorption or emission wavelength of the dye). This provides the potential for the development of a cost-effective, low-power and portable sensor for detection of dissolved CO₂ for a variety of applications.

2. Experimental

2.1. Composite sensing material preparation

The procedure of the CO₂-sensitive ion pair preparation is based on the previously published work [11,19]. The ion pair consisted of a pH-sensitive dye (either cresol red or pyranine) and an organic quaternary cation as an ion-pairing agent. The dye containing solution (S1) was prepared by dissolving either 25 mg of cresol red (Aldrich) or 50 mg of pyranine (Aldrich) in 22.5 mL of 0.1 M NaOH. The quaternary cation solution (S2) was prepared by dissolving 37.4 mg of tetraoctylammonium bromide (TOABr, Aldrich) in 3 mL of toluene [11,19]. Solutions S1 and S2 were mixed and stirred for 5 min and the organic phase was removed and washed twice with 3 mL of 0.1 M NaOH. The resulting organic phase contained the pure ion pair of either [cresol red⁻/TOA⁺] or [pyranine⁻/TOA⁺] dissolved in toluene. Tetraoctylammonium hydroxide (TOAOH) was prepared by stirring 1.37 g of TOABr with 1.16 g of silver oxide (Aldrich) and 10 mL of methanol for 5 h. The solid phase (silver bromide) was then removed. The ion pair encapsulation was done according to the following procedure: 1 mL of TOAOH, 1 mL of the previously prepared ion pair solution in toluene, 2 mL of toluene and 560 mg of anion exchange resin microbeads (Dowex[®] chloride form, ~40–80 μm, Sigma–Aldrich) were mixed for 1 h. The resulted suspension was dried in the oven at 50 °C overnight in order to evaporate the toluene. The dry powder was dissolved in 5 ml of ethanol and 5 ml

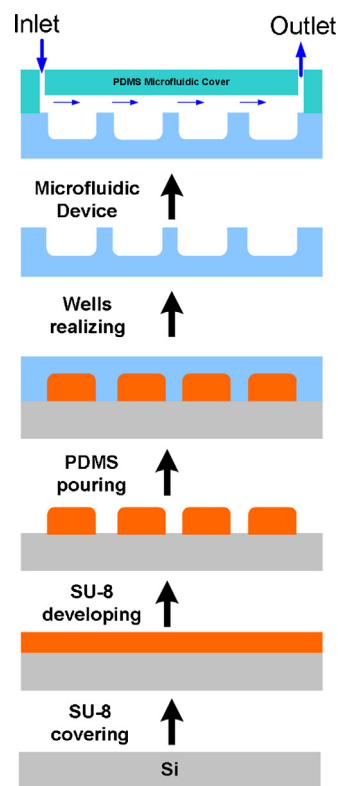


Fig. 1. Microfluidic device fabrication.

of water was subsequently added. The basic chemical mechanism of the ion pair sensitivity to CO₂ is based on the reaction between the dissolved CO₂ and the quaternary ammonium cation of the ion pair (Eq. (1)) which leads to protonation of the dye molecule, resulting in a change in its absorbance properties [11,19].

2.2. Microfluidic device fabrication

Fig. 1 shows the main steps of the device fabrication process. A mask with desired master features (an array of microwells, Fig. 2b–d) was previously fabricated. 1 ml of a photoresist SU-8 2100 (for microfluidic channels fabrication) or SU-8 2150 (for microwells fabrication) was spin-coated on the clean 4 in. wafer, followed by soft bake at 65 °C for 30 min and, subsequently, at 95 °C for 90 min. The wafer was then placed into the OAI Model 204 mask aligner and exposed to 365 nm light with 20 mW/cm² energy dose for 30 s, followed by post-exposure bake at 65 °C for 5 min and, subsequently, at 95 °C for 20 min. The wafer was developed in the SU-8 developer (propylene glycol monomethyl ether acetate) for ~25–30 min. After the development, the wafer was rinsed with isopropanol and dried using nitrogen gun. Finally, the desired master features, i.e. either 500 μm diameter × 500 μm thickness circular steps for PDMS wells mold or 2 cm length × 600 μm width × 200 μm thickness of rectangular steps for PDMS channels mold were formed on top of the wafer. The base/curing agent ratio (of the PDMS pre-polymer components) was 10:1. The prepared PDMS mixtures were first placed in a vacuum desiccator for 30 min for degassing and then poured on top of the master, followed by vacuum degassing for 30 min. The master was then placed inside an oven at 70 °C for 4 h to cure the device layer. The PDMS mold was cut around the edge of the master wafer and peeled up. Fluid inlet and outlet holes of the PDMS device were punched using a 16 gauge needle before placing it into the reactive ion etcher (RIE) chamber. The March CS-1701F RIE was used (50 mT). Oxygen was flowed for 30 s at 50 W RF power. Immediately after removing from the RIE

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