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Plug and Play Colorimetric Carbon Dioxide Sensor

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Abstract. Carbon dioxide measurement is an important endeavor in many industries such as food packaging, grain storage and health industry. This work presents a reversible, plug and play and low-cost colorimetric CO_2 sensor calibrated in a proper concentration ranging from 1% to 3% of CO_2. The sensor showed potential for improvement to increase resolution, for measuring lower CO_2 concentrations and for more accurate readings.

1. Introduction

The Earth's atmosphere is made up mostly of Nitrogen (N_2 - 78.08%), Oxygen (O_2 - 20.95%) and Argon (Ar - 0.93%), the remainder being formed by other gases, led by Carbon Dioxide (CO_2- 0.04%) [1]. The monitoring of atmospheric CO_2 is currently one of the main topics on the table of several governments and environmental associations. For the last 200 years, the atmospheric concentration has increased from 280 parts per million(ppm) to 400 ppm.
In 2019, the market size for gas sensors was valued at around 823.1 million$[2]. This means that gas sensors are sought out from both private and public perspectives. For carbon dioxide sensors in specific, there are many industries that need accurate, small, and robust sensors for real time monitoring in a wide variety of applications.

Nowadays, there is a high demand for safe, healthy, and fresh food to be delivered at command. In modified atmosphere packaging, food is packaged, and sealed, inside an altered atmosphere, where carbon dioxide is used has a control factor to protect the food from spoils, pathogens and to extend shelf life.[3]

In this work, an optical sensor for CO_2 monitoring is presented based on the absorption of a sensitive membrane with an accurate reading obtained through optoelectronic components in a specially designed configuration.

2 Materials and Methods

2.1. Sensing Membrane

A CO_2 sensor was built around a colorimetric membrane manufactured with the following chemical reagents: p-nitrophenol (pNPh) (Sigmal-Aldrich ReagentPlus, >99%), the pNPh was used as a starting monomer for the synthesis of the poly pNPh(NP), tetraethylammonium hydroxide solution (TOA-OH; 20% in methanol, Sigma-Aldrich) was used as a quaternary ammonium (TOA-OH), Hydrogel D4 (Advance Source Biochemicals) was used as polymer to produce a homogeneous membrane, and Sylgard 184(Dow Corning, 10:1, Midland, MI, USA) was used to encapsulate and protect the chemical membrane following the procedure from[4].

For the colorimetric membrane development, a chemical cocktail was prepared by dissolving 5 mg of poly p-nitrophenol (NP) in 0.05 ml of a MeOH:H2O(1.5:1) mixture followed by the addition of 0.5 ml of a 0.5 M TOA-OH solution. After total dissolution, it was added 0.1 ml of Hydrogel D4 solution (10% in Ethanol,96%) and the resulted solution was stirred for a few minutes. The final cocktail was then spread on a mylar foil by spin-coating (900rpm for 60 seconds) and then left to dry for about two hours at room temperature and stored in the fridge prior to use.

The sensing dye chemistry is based on an ion-pair formation resulted from the interaction of the quaternary ammonium and the colorimetric polymer (TOA^+NP^-), keeping the sensitive dye in its anionic form. The interaction with the gaseous CO_2 is linked to the association of a few molecules of water ($TOA^+NP^-.xH_2O$) that come from air humidity. Equation 1 describes this process.

$$TOA^+ + NP^-.\chi H_2O + CO_2 \leftrightarrows TOA^+HCO_3^-.(\chi-1)H_2O.HNP \quad (1)$$

2.2. Sensing prototype

The prototype presented in figure 1 is based on the absorbance measurements of the sensing membrane through the transmission of a light signal from a white LED (model c503d, Cree, United Kingdom) towards to an RGB photodetector (model s9032-02, Hamamatsu, Japan) using two collimating lenses. This light signal is then acquired in the photodetector which is wavelength selective in three distinct bands with embed spectral filters corresponding to red (630 nm), green (555 nm) and blue

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(450 nm). The absorption band of the sensing membrane due to the CO_2 absorbance is at 470 nm so the blue band is used for the sensing signal while the red band is used for the reference signal. Each light signal is converted into a current, amplified and digitalized locally. The digital information is processed in real time in a computer using a LabVIEW software.

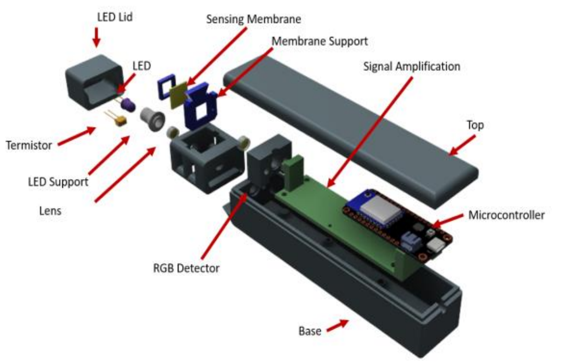

Fig. 1. Exploded view of the sensing prototype showing all the internal components

2.3. Measurements

The sensor works by detecting specific absorption variations of the chemical membrane in reaction with CO_2. As the gas concentration of CO_2 increases, an internal reaction occurs in the membrane, decreasing its pH. Depending on its internal pH levels the membrane, with a strong yellow color, becomes colorless as the pH increases and recovers its color as the pH decreases.

The sensor was tested in the setup illustrated in Figure 2, by injecting CO_2 and nitrogen (N_2) controlled by mass-flow controllers (Brooks, SLA5800 Series; Hatfield, PA, USA), in a gas mixture vessel before performing the measurements in the measurement chamber. Between controlled concentrations the gas inside the chamber was removed by injecting N_2 which pushes the remaining gas out of the chamber, as a base line atmospheric CO_2 was used. This process was repeated for each injected concentration.

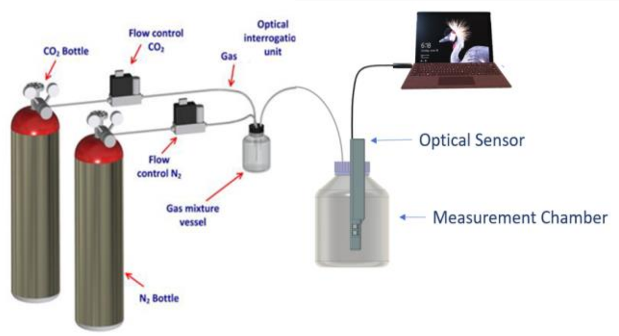

Fig. 2. Measurement setup (Adapted from[4])

3 Experimental Results and Discussion

The sensor was evaluated in controlled atmosphere and a preliminary calibration was done for 1, 2 and 3% of CO_2 in pure N_2. The signal from the white LED crosses the sensing membrane and is acquired by the RGB. Figure 3 (a) shows the time response of the sensor placed in the measurement setup for different concentrations of CO_2 and repeated in time. After each cycle the measurement chamber was filled with atmospheric gas.

The Blue/Experimental signal is used to perform the CO_2 measurement, while the red signal is only used as a reference signal to eliminate external fluctuations in real-time. The reference signal shows the stability of the LED, while correcting any external factors that could affect the whole signal. All signals have a logarithmic behavior for the three CO_2 concentrations, so a logarithm of base 10 was applied to the X axis to enable linear response.

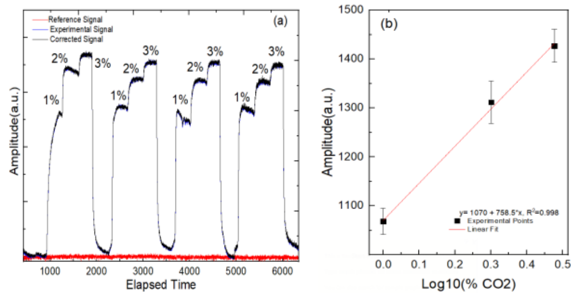

Fig. 3. (a) Sensor reaction with different CO_2 concentrations (1%, 2% and 3%). Experimental signal is used as a measurement signal, and Reference signal was used to correct of any external fluctuations (b) Sensor calibration curve plotted as a function of the logarithm percentage of CO_2 concentration.

The preliminary results from figure 3 have shown a potential for higher resolution measurement, with smaller concentration steps in between, more accurate readings and with a potential to measure lower levels of CO_2.

The gaseous carbon dioxide sensor was developed in a plug and play configuration to be used in real-time monitoring. With more improvements the sensor can be used in more challenging environments.

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