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Colorimetric Inks: A New Approach to Low Cost and Disposable Gas Sensors: The Case of Formaldehyde

Maria González-Gómez[1], Anna Zymohliad[1], Ismael Benito-Altamirano[1], Joan Daniel Prades[2], Olga Casals[1], and Cristian Fàbrega[1].

[1] Dept. of Electronics and Biomedical Enginering, University of Barcelona, Marti i Franques 1, Barcelona, Spain.

[2] Institute of Semiconductor Technology (IHT) and Laboratory for Emerging Nanometrology (LENA), Technische Universität Braunschweig, Hans-Sommer Str. 66, D-38106 Braunschweig, Germany

cfabrega@ub.edu

Summary:

Indoor air quality (IAQ) is a major health concern, and monitoring pollutants indoors is crucial. Current technology offers expensive and bulky options or cheap sensors with limited detection capabilities. New sensor technologies are being developed, but most focus on size and power consumption, neglecting the ability to definitively identify pollutants. Colorimetric sensors offer excellent specificity for detecting target pollutants. In this talk we will discuss the latest developments and limitations of colorimetric sensors and explore possibilities for future sensor technology.

Keywords: Gas sensors, colorimetric sensors, indoor air quality, formaldehyde, CO2

Introduction

Colorimetric sensors offer exceptional selectivity for detecting specific gaseous molecules. This advantage, stemming from the targeted response of colorimetric indicators to specific wavelengths of light, makes them highly attractive for gas detection applications. However, traditional readout methods pose significant limitations.

The development of miniaturized systems for continuous colorimetric sensor readout presents a critical challenge. Existing efforts utilize light sources and photodetectors to measure changes in absorbance, reflectance, or transmittance at specific wavelengths. These configurations often involve complex integration of components, particularly concerning optical alignment. Additionally, miniaturization can hinder the ability to refresh the indicator material once it degrades.

This work presents a novel approach for continuous readout of colorimetric gas sensors. Our design prioritizes simplicity and versatility by utilizing readily available, commercially accessible components. This approach offers several key advantages: i) Accessibility: Utilizing commercially available components reduces cost and simplifies construction; ii) Wavelength Compatibility: The design is compatible with a wide range of colorimetric indicators operating at different wavelengths; iii) Resettability/Refreshability: The system allows for easy resetting or refreshing of the indicator material, overcoming a major limitation of miniaturized colorimetric sensors and; iv) Repeatability: The design ensures excellent repeatability of measurements across different sensor units.

This paper details the design, implementation, and performance evaluation of our proposed approach. We believe this simple and versatile method has the potential to significantly advance the field of continuous colorimetric gas sensing. For a rigorous test of our approach's capabilities, we chose formaldehyde, one of the most challenging pollutants for indoor air quality (IAQ) applications. Our results demonstrate that our simple approach offers excellent performance, including high selectivity against interfering gases, excellent reproducibility, and reliable operation.

Experimental

Our approach is based on a readily available and inexpensive component called the MAX30105. This component emits light in three different wavelengths (green, red, and infrared) and measures the amount of reflected light at each wavelength using a broad band photodiode. The small size and low cost of this component make it ideal for use in miniaturized colorimetric gas sensors.

The colorimetric sensor utilizes a previously reported ink formulation [1]. This ink changes color due to a reaction between a primary amine and formaldehyde, which alters the solution's pH. A standard pH indicator dye, Bromoxylenol blue, visually reflects this pH change.

Results

The colorimetric sensor operates based on the chemical reaction between a primary amine and formaldehyde. This reaction, known as nucleophilic addition, forms an imine molecule and releases a water molecule. Importantly, under these conditions, the reaction is irreversible. As a result, the color change of the dye intensifies as it is exposed to increasing amounts (doses) of formaldehyde, until a saturation point is reached (Fig. 1). Our experiments revealed that the sensitivity and durability of the sensor depend on the formulation, particularly the amount of amine and the thickness of the printed film. Lower amine concentrations resulted in higher sensitivity but faster saturation. Conversely, higher amine concentrations offered slower saturation but reduced sensitivity. To achieve optimal performance, we formulated the colorimetric sensor to strike a balance between these two factors.

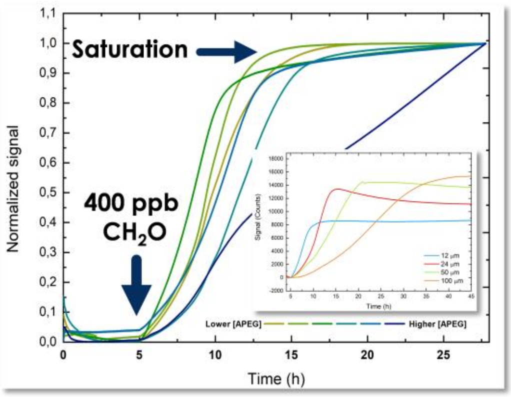

Fig 1. Dosimeter expeirments and ink formulation tunning.

Although the overall color change of the ink is irreversible, we observed that the rate of color change is directly proportional to the formaldehyde (CH_2O) concentration during exposure (Fig. 2). This means the steeper the initial slope of the color change, the higher the CH2O concentration. By exploiting this property, we can analyze the rate of color change, or the first derivative of the signal (Fig. 2, insert), to determine the CH_2O concentration. Using this approach, we achieved a detection limit of 85 ppb for CH_2O.

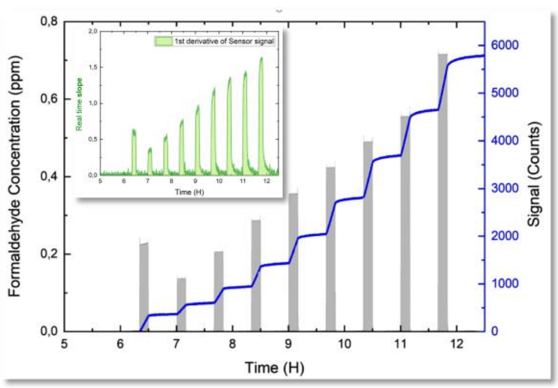

Fig. 2. Transient measurements signal at different CH_2O concentration and the 1st derivative of the signal.

Figure 3 depicts a calibration curve constructed using eight samples from three distinct batches. The data demonstrates a strong linear relationship between the response and formaldehyde concentration, with minimal deviations considering the use of diverse samples. We further validated this calibration model by performing a new transient experiment with a fresh sample. The predicted concentration by the model closely matched the nominal concentration, confirming the model's accuracy.

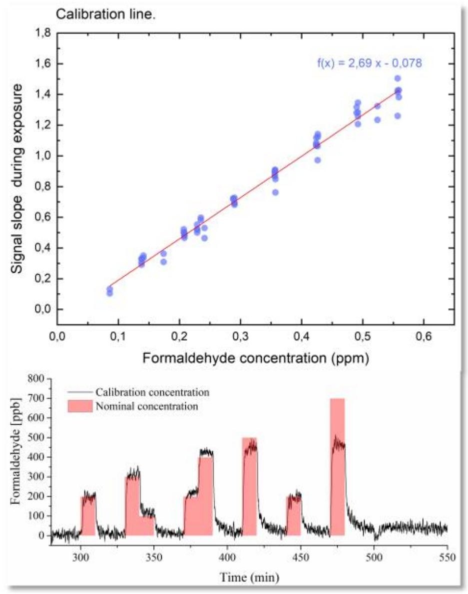

Fig. 3. Calibration line and test validation experiment.

Finally, we investigated the potential interference from common indoor air pollutants: moisture, nitrogen dioxide (NO_2), carbon dioxide (CO_2), and carbon monoxide (CO). Experiments were conducted by exposing the sensor to each interferent gas at various concentrations alongside a fixed concentration of formaldehyde. The results reveal that relative humidity slightly interferes with the sensor response at both low and high humidity ranges. Conversely, no significant interference was observed within the model's calibration error range for CO and CO_2. NO_2, however, exhibited a clear interference effect, causing significant deviations from the expected formaldehyde value. It's important to note that the NO_2 concentrations used in the experiments were 4 to 20 times higher than typical indoor air levels.

[1] Feng, L.; Musto, C. J.; Suslick, K. S. A Simple and Highly Sensitive Colorimetric Detection Method for Gaseous Formaldehyde. J. Am. Chem. Soc. 2010, 132 (12), 4046–4047. https://doi.org/10.1021/ja910366p.