A Room Temperature Operated Carbon Dioxide Sensor Based on EB-PANI/PEDOT:PSS Sensing Material

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Abstract—To resolve the high power consumption and complex polymerization process of most CO₂ sensors, a room temperature operation CO₂ sensor based on Emeraldine base-polyaniline (EB-PANI) blended with poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) was developed. In this work, the sensor performed linear response to CO₂ in working range of 1000-20000 ppm with the response from 0.98% to 3.83%. This detection range is low enough for environmental detection. On the other hand, compared to the response to CO₂, this sensor has considerably lower response to humidity, from 50 % to 85 % RH. Hence, in the ambient environment, this CO₂ sensor is not affected by humidity when detecting the CO₂ concentration.

Keywords—CO₂ sensor; polyaniline; PEDOT:PSS.

I. INTRODUCTION

CO₂ is a common gas in our life and plays an important role for agriculture [1], indoor air quality [2], food storage [3], etc. For indoor air quality, the safe CO₂ concentration range is between 1500 ppm and 5000 ppm. A higher concentration would lead to people feeling sleepy, having headaches, inattention [2] and so on. Furthermore, it has been proven that, by integrating a CO₂ sensor into the ventilation system, the ventilating strength level can be adjusted depending on the CO₂ concentration. This makes the ventilation system more efficient and can reduce about 10%-30% of energy consumption and ventilation loads [4]. On the other hand, in health care, a CO₂ sensor can be used to monitor patients respiratory capacity, and, hence, lung condition. The general standard is from 4% to 6%, or the patient might be under the risk of metabolic acidosis or respiratory failure.

Based on these important applications, many researchers developed various new sensing materials for CO₂ sensing, such as copper oxide and spinel ferrite nanocomposite [5], LaFeO₃ [6] and other metal oxide of nanocomposite [7]. However, metal oxide based sensors need to operate at high temperature, which are from 150°C to 300°C, and this requires a large energy consumption. Therefore, other research works focus on polymer-based materials to avoid this problem, such as PEDOT [8], RGO [9], and PANI [10]. However, the chemical inertness of carbon dioxide has caused many difficulties in developing polymer base CO₂ chemical sensors [11]. For example, RGO sensor needs high voltage plasma treatment to recover the sensing feature after measurement [9]; SPAN sensor’s detection limit is too high (20000ppm) and the polymerization process is complicated [12][13]; PEDOT and PANI sensors need to detect CO₂ with high humidity to improve the sensitivity [8][10]. Therefore, for environmental CO₂ detection, these problems still need to improve.

In this work, Emeraldine base-polyaniline (EB-PANI) blended with poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) was used to be a sensing film. In Oleg P Dimitriev ed. Al. study [14], the authors claimed that the blending of PEDOT:PSS can improve PANI’s conductivity because of PSS’s co-doping in PEDOT and EB-PANI. According to previous research, it was expected that the blending of PEDOT:PSS can also increase the water absorption ability compared to pure EB-PANI and then increase bicarbonate formation [15]. Furthermore, it was also expected that the PSS co-doping will cause the sulfonic acid polyaniline (SPAN). Based on the assumption, EB-PANI/PEDOT:PSS would be an appropriate sensing material for indoor CO₂ monitoring.

The remainder of this paper is structured as follows. In Section II, the fabrication process and measurement steps are described. In Section III, the sensing result and the humidity effect are discussed. We conclude in Section IV.

II. EXPERIMENT AND MEASUREMENT

This experiment is composed of two parts, one is the fabrication process of sensing film and substrate; the other is measurement system set-up and method.

A. Sensor fabrication

A p-type wafer with 300 nm oxide on the top of surface was used as the device substrate. The substrate was cleaned
by acetone and isopropyl alcohol. After that, the substrate was dry out by heating and \( \text{N}_2 \) gas to remove humidity. This was followed by photolithography. The electrode was defined with W/L in the ratio of 800 um/40 um. Then, the sensing electrodes, i.e., 20 nm/200 nm of Cr/Au electrodes, were achieved by e-gun evaporation and lift-off process.

First, EB-PANI powder was dissolved in N-methylpyrrolidinone (NMP) to prepare a stock solution with concentration of 1 wt.%. Then, 1 w.t.% of PEDOT:PSS aqueous solution was added slowly into 1 w.t.% of EB-PANI solution in 1:1 proportion (v/v). After adding materials into solutions, the blended solution was mixing well by stirring. Finally, the sensing film was fabricating by drop-casting, and baking in dynamic vacuum for 24hr in 60°C. Figure 1 shows the structure of EB-PANI and PEDOT:PSS. In our assumption, this mixing will make the EB-PANI reform to Sulfonic Acid polyaniline (SPAN), which will change the working range for environmental monitoring [12].

![Figure 1. Structure of sensing material: EB-PANI and PEDOT:PSS, and SPAN.](image)

### B. Measurement system

To measure the response of the developed sensing material, the LCR meter, Agilent E4980A, provides DC 1V to measure the resistance of the sensing film. Figure 2 shows the measurement system. The gas sensing experiment was operated in the chamber. Before gas sensing, the chamber was vacuumed by a mechanical pump for 5 minutes to remove the ambient gas; the vacuum level was below 0.2 torr. After that, the dry air (79% \( \text{N}_2 \) and 21% \( \text{O}_2 \)) was flown into the chamber for 3 minutes, then, the vacuum process was repeated. After removing dry air by vacuuming for 5 minutes, \( \text{CO}_2 \) with dry air was then flown into the chamber and, next, we waited for 5 minutes.

In order to simulate the real life environment, \( \text{CO}_2 \) detection was measured in various relative humidity conditions. Therefore, Deionized water (DI water) was inkjeted and flown in with dry air and \( \text{CO}_2 \). The water fully vaporizes. The relative humidity concentration was detected from a commercial humidity meter. All the measurements were carried out at room temperature.

The \( \text{CO}_2 \) concentration in chamber was controlled by Micro Fluid controller (MFC). 500 ppm \( \text{CO}_2 \) (background is dry air) is a reference gas, then \( \text{CO}_2 \) and dry air flow rate were controlled to adjust the \( \text{CO}_2 \) concentration. Each concentration of \( \text{CO}_2 \) with different humidity was staying in chamber for 3 minutes then removed by vacuum. During measurement, the pressure in the chamber was controlled to be the same as the ambient pressure. Finally, the measured data was recorded by a LabView program.

### III. RESULTS AND DISCUSSION

In the following, \( \text{CO}_2 \) sensitivity and humidity effects are discussed separately.

#### A. Gas sensing properties

In the case of \( \text{CO}_2 \) sensing mechanism, Tsuyoshi Tonosaki ed al. [16] claimed that the hydrolysis of \( \text{CO}_2 \) will generate bicarbonate ions, and be incorporated to EB-PANI, which will then become emeraldine salt-PANI (ES-PANI). The ES-PANI is more conductive than EB-PANI. Therefore, the higher \( \text{CO}_2 \) concentration, the more bicarbonate ions will be generated and cause the EB-PANI transforming into ES type, resulting in the decreasing of the sensing material resistance.

Based on the theory, the response is defined as the following equation:

\[
\text{response} (%) = \frac{R_0 - R_{\text{CO}_2}}{R_0} \times 100\%
\]

where \( R_0 \) represents the resistance of sensor in the reference gas. Since the resistance decreased with the rising of \( \text{CO}_2 \) concentration, the sensitivity can be defined. For a normal indoor ambient environment, the \( \text{CO}_2 \) concentration is around 500 ppm and humidity is between 65% RH and 75% RH. Therefore, in our measurement, we kept the humidity in this range and 500 ppm \( \text{CO}_2 \) was assumed as the reference gas.

Figure 3 shows the resistance of EB-PANI/PEDOT:PSS sensor decreases when a higher concentration of \( \text{CO}_2 \) with flow in (with vaporized water). As the \( \text{CO}_2 \) concentration
increases, the resistance decrease, so we can clearly distinguish different concentration of CO$_2$. The details of the resistance variation are shown in Table 1. In this table, the response time can be observed, which is around 40 seconds and the recovery time is around 250 seconds. Figure 4 is the sensor response to different CO$_2$ concentrations, which are from 1000 ppm to 50000 ppm. The result shows that the maximum response is at 20000 ppm with response of 3.83%. The linear working range is between 1000 and 20000 ppm. As CO$_2$ concentration is higher than 20000 ppm, the response will saturate. For environment CO$_2$ detection, this working range is appropriate for indoor environmental monitoring.

### Table I. Resistance Value in Figure 3.

<table>
<thead>
<tr>
<th>CO$_2$ concentration (ppm)</th>
<th>Resistance(Ω)</th>
<th>response</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>477.4k</td>
<td></td>
</tr>
<tr>
<td>20000</td>
<td>462.0k</td>
<td>-3.21%</td>
</tr>
</tbody>
</table>

Therefore, the humidity effect is shown in Figure 5. The sensor responses to humidity from 50% RH to 85% RH are much smaller compared to CO$_2$ response, and there is also no obviously trend of humidity effect. Hence, in ambient environment, this CO$_2$ sensor can ignore the humidity effect to detect CO$_2$ concentration. Differences in the original resistance of every sensor would due to process variations, such as blending quality, and the relation of standard variation and resistance still need to be studied.

### IV. CONCLUSION

In this paper, a room temperature operated CO$_2$ sensor has been developed with a simple fabrication process. The detection range is from 1000 ppm to 20000 ppm with highly response from 0.98% to 3.83%. It is appropriate for environmental CO$_2$ detection. Furthermore, the humidity effect is also discussed. Compared to CO$_2$ sensitivity, this sensor has extremely low response for humidity. Hence, the blending of PEDOT:PSS into EB-PANI is successfully resolving the problem of humidity effect for most polymer based materials. This CO$_2$ sensor is highly potential for indoor environmental detection.
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