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 CO_2 sensors, a room temperature operation CO_2 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 CO_2 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 CO_2, this sensor has considerably lower response to humidity, from 50 % to 85 % RH. Hence, in the ambient environment, this CO_2 sensor is not affected by humidity when detecting the CO_2 concentration.**

Keywords-CO_2 sensor; polyaniline; PEDOT:PSS.

I. INTRODUCTION

CO_2 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 rage 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 CO_2 sensor into the ventilation system, the ventilating strength level can be adjusted depending on the CO_2 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 CO_2 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 CO_2 sensing, such as copper oxide and spinel ferrite nanocomposite [5], $LaFeO_3$ [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 CO_2 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 CO_2 with high humidity to improve the sensitivity [8][10]. Therefore, for environmental CO_2 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 CO_2 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

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by acetone and isopropyl alcohol. After that, the substrate was dry out by heating and 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].

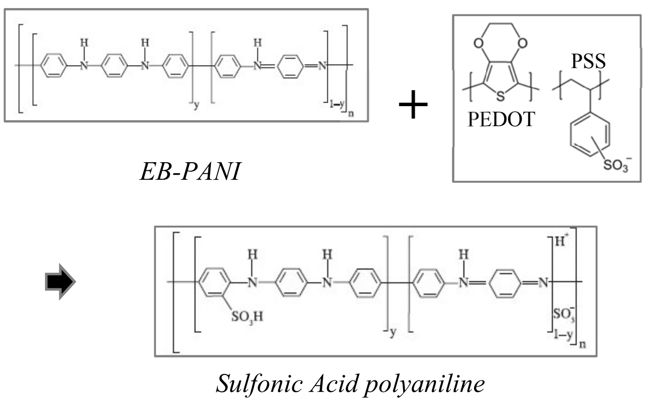

Figure 1. Structure of sensing material: EB-PANI and PEDOT:PSS, and SPAN.

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% N_2 and 21% 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, 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, CO_2 detection was measured in various relative humidity conditions. Therefore, Deionized water (DI water) was ink-jeted and flown in with dry air and 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.

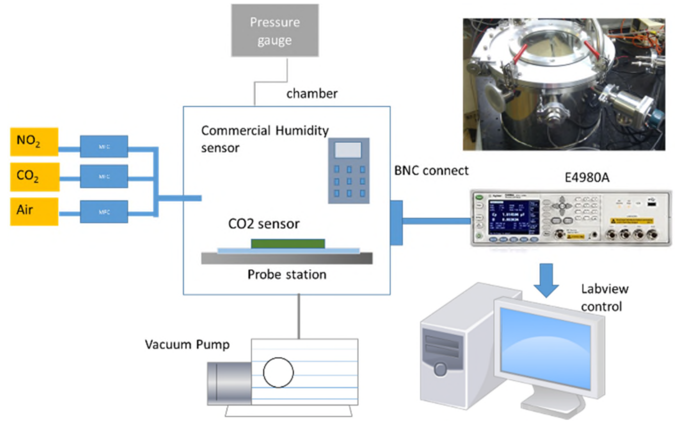

Figure 2. The schematic diagram for gas sensor measurement

The CO_2 concentration in chamber was controlled by Micro Fluid controller (MFC). 500 ppm CO_2 (background is dry air) is a reference gas, then CO_2 and dry air flow rate were controlled to adjust the CO_2 concentration. Each concentration of 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, CO_2 sensitivity and humidity effects are discussed separately.

A. Gas sensing properties

In the case of CO_2 sensing mechanism, Tsuyoshi Tonosaki ed al. [16] claimed that the hydrolysis of CO2 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 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:

$$\text{response}\ (\%) = \frac{R_0 - R_{CO2}}{R_0} \times 100\%$$

where R_0 represents the resistance of sensor in the reference gas. Since the resistance decreased with the rising of CO_2 concentration, the sensitivity can be defined. For a normal indoor ambient environment, the 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 CO2 was assumed as the reference gas.

Figure 3 shows the resistance of EB-PANI/PEDOT:PSS sensor decreases when a higher concentration of CO_2 with flow in (with vaporized water). As the CO_2 concentration

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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.

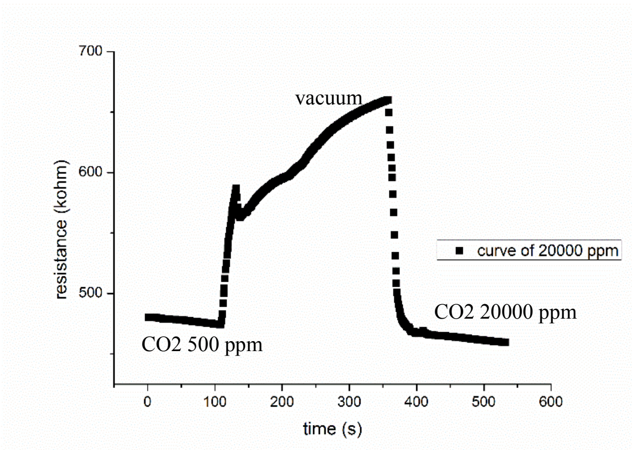


Figure 3. CO_2 response curve of EB-PANI/PEDOT:PSS sensor in humid environment, the humidity was controlled at 70±5% RH. The step of single concentration response measurement is: 1) flow the 500 ppm CO_2 in RH 70%, 2) vacuum the chamber 3) flow the 20000 ppm CO_2 in RH 70%, too.

TABLE I. RESISTANCE VALUE IN FIGURE 3.

CO2 concentration (ppm)	Resistance(Ω)	response
500	477.4k	
20000	462.0k	-3.21%

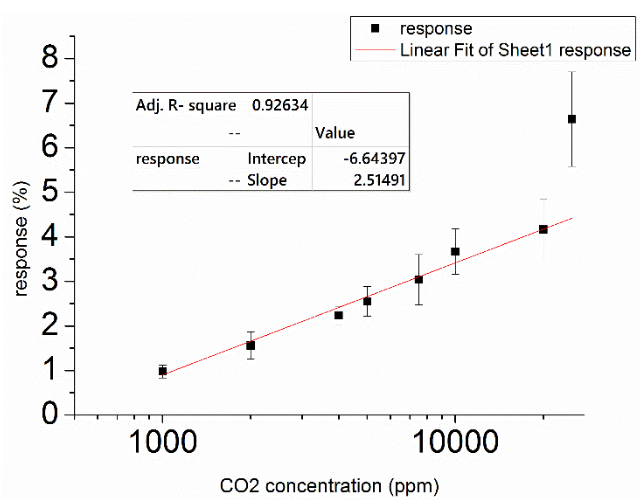
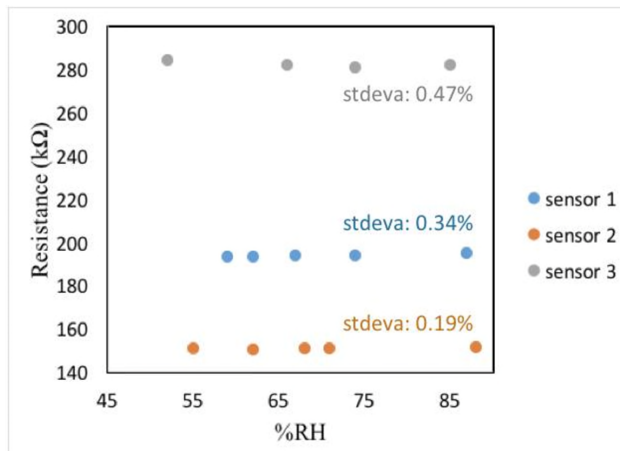


Figure 4. CO_2 response from 1000 to 50000 ppm, which humidity is controlled at 70±5% RH.

B. Humidity effect

For past CO_2 polymer base sensors, most of them significantly depend on the humidity value and need to detect CO_2 with high humidity concentration. However, compared to CO_2 sensitivity, these sensing films showed much higher sensitivity to humidity. To resolve this problem, the hydrophilic material, PEDOT:PSS, was blended into EB-PANI. With this method, it can improve the formation of bicarbonate to enhance CO_2 detection, but improve the selectivity to humidity. Due to the opposing conductivity variation trend of PEDOT:PSS and PANI, in summation the response to humidity was assumed to offset each other then become stable.



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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