DOI 10.5162/EUROSENSORS2025/T5.1.4

Room Temperature CO_2 Gas Sensor Based on Carbon Polymer Dots - PEDOT:PSS Composite Thin Film

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Summary

A green synthetic method was developed to produce carbon polymer dots with a high content of amino groups. A composite material, obtained dispersing the synthetized dots in the conductive polymer matrix PEDOT:PSS (Poly(3,4-EthyleneDiOxyThiophene) PolyStyrene Sulfonate), was used to fabricate a low-cost, flexible chemiresistive gas sensor for CO_2 detection in the concentration range 150-3000 ppm. The sensor device showed high response and good repeatability upon CO_2 exposure at room temperature with negligible responses towards CO. Being a stronger Lewis acid, the CO_2 can accept lone pairs of electrons from amino groups on carbon dots surface.

Keywords: carbon polymer dots, gas sensors, chemiresistive sensors, interdigitated electrodes, flexible electronics.

Introduction

The monitoring of CO_2 has great relevance for environmental protection and global warming control. Being the combustion product of fossil fuel, solid waste and other biologic materials, CO_2 is considered the main greenhouse gas responsible for climate change. The CO_2 measurements also play a crucial role for many industrial uses such as food packaging, carbonation of beverages, and fertilizer production. In addition, to ensure safety in workplaces and in all confined indoor spaces the maximum amount of CO_2 should be in the range 350-800 ppm. Higher concentrations can induce headaches, sore throat and nasal irritation [1]. Currently, CO_2 sensors are mostly based on rigid ceramic materials that require a high operating temperature. In present study a composite material, obtained dispersing Carbon Polymer Dots (CPDs) in the conductive polymer matrix PEDOT:PSS, was used to fabricate a low-cost, flexible chemiresistive gas sensor for CO_2 detection at room temperature. CPDs are promising low-cost materials, generally produced with simple synthesis methods, and results superior to traditional semiconductor quantum dots for robustness, chemical inertness, and biocompatibility, being non-toxic compounds that do not contain metals [2]. The proposed sensor, based on CPDs - PEDOT:PSS composite, showed high responses and good repeatability upon CO_2 exposure with negligible responses towards interfering CO molecules.

Materials and methods

The dipicolinic acid, chosen as precursor for CPDs, was mixed to an excess of freshly distilled ethylenediamine without solvent addition. The CPDs were obtained by applying a steady temperature of 300°C for 30 minutes in a microwave reactor. Finally, ethanol was added on the crude reaction mixture and the solid carbon nanoparticles were separated through centrifugation for 5 min at 1000 rpm. The carbon dots were recovered by water dissolution. To fabricate the sensor device, a water solution of CPDs and PEDOT:PSS with weight ratio 1:1 was dropped on flexible substrate made by PolyEthylene Terephthalate (PET), previously coated with inkjet-printed interdigitated electrodes in silver (Ag). The chemiresistive sensor was located in a sealed stainless cell and exposed to synthetic air (reference gas) and to several dilutions of CO_2 in dry air keeping the flow rate constant as 1000 sccm.

Results

With the aim to produce nitrogen rich CPDs, a precursor containing a pyridinic nitrogen moiety, as the dipicolinic acid, and an excess of ethylenediamine were selected as starting reagents. A composite material, obtained dispersing the synthetized CPDs in the conductive polymer matrix PEDOT:PSS, was used to fabricate a chemiresistive gas sensor for CO_2 detection in the concentration range 150-3000 ppm at room temperature. Typical gas detecting curves, reported in Figure 1, put in evidence an increase of electrical resistance upon exposure to 1000, 500 and 250 ppm of CO_2. Being a Lewis acid, the chemisorbed CO_2 can accept lone pairs of electrons from nitrogen atoms on CPDs surface, reducing the number of major charge carriers, and consequently increasing the electrical resistance.

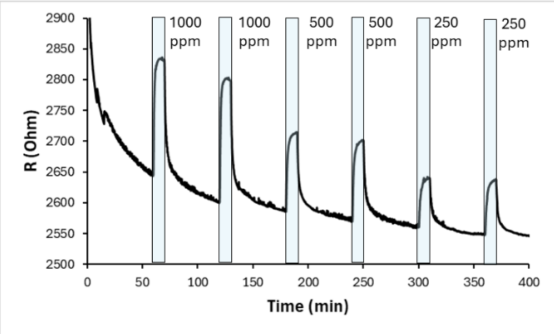

Fig. 1. Sensor resistance versus time upon exposure of decreasing CO_2 concentrations of 1000, 500 and 250 ppm at room temperature.

The sensor response (SR%) was calculated by the following relationship:

$$SR\% = \left(\frac{Rg-Ra}{Ra}\right) * 100 \qquad (1)$$

where R_g and R_a are the electrical resistance measured with exposure to gas and air, respectively. The logarithmic fitting curve of SR% versus CO_2 concentration was reported in Figure 2. The sensor response versus the logarithm of concentration can well fitted by a straight line in the investigated concentration range 150-3000 ppm (inset of Fig. 2). No sensor responses were recorded in an analogous device fabricated with pure PEDOT:PSS films.

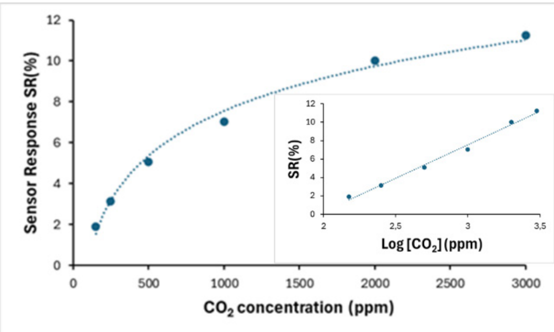

Fig. 2. Sensor response versus gas concentration and sensor responses versus the logarithm of concentration in the inset.

As additional relevant indicators of device performances, the response time and the recovery time were calculated considering the required time to reach 90% of the maximum response under CO_2 exposure and the 10% under reference gas exposure, respectively. An average value of 160 sec was calculated as response time, while the recovery time was almost double. No significant responses were obtained exposing the same sensor to several CO concentrations. The amino groups on CPDs surface selectively interact with CO_2 that is a stronger Lewis acid. The acid-base reactions between the amino groups and CO_2 promote the formation of ions such as carbamates and bicarbonates, which in turn, contribute to change in the resistance of the sensor active layer. Repeated exposure test at 2000 ppm of CO_2, showed in Figure 3, demonstrated the good stability of the baseline resistance and the good reproducibility of measurements.

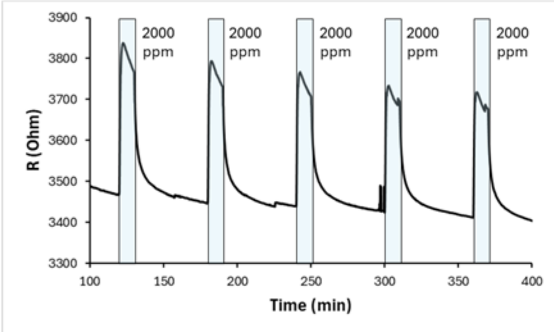

Fig. 3. Five repeated exposure tests at 2000 ppm of CO_2.

Conclusions

In summary, a green synthetic method was developed to produce nitrogen rich CPDs and a chemiresistive flexible sensor to monitor CO_2 at room temperature was fabricated by using a CPDs - PEDOT:PSS composite material. The sensor device showed high responses and repeatability upon CO_2 exposure in the large concentration range 150-3000 ppm with negligible sensitivity towards CO. The presented data highlighted the CPDs potential in sensing applications. Due to the simple design and fabrication process, the described sensor could lead to the implementation of flexible wearable devices suitable for air quality monitoring in confined workspaces such as mines and manufacturing facilities including indoor monitoring.

References

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Acknowledgements

This study was funded by project SENSAIR (*Gas SENSing solutions for smart AIR monitoring applications)* granted by Italian PNRR cascade call SAMOTHRACE - Next Generation EU.