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Solid State Gas Sensor Based on Polyaniline Doped with [3,3′-Co(1,2-C2B9H11)2]−1 for Detection of Acetone: Diagnostic to Heart Failure Disease †

Abhishek Sonu [1,*], Abdoullatif Baraket [1], Selim Boudjaoui [1], Juan Gallardo [1], Nadia Zine [1], Monique Sigaud [1], Marie Hangouet [1], Albert Alcácer [2], Angelos Streklas [2], Joan Bausells [2] and Abdelhamid Errachid [1]

[1] Institut des Sciences Analytiques, Université de Lyon, UMR 5280, CNRS, Université Lyon 1, ENS Lyon−5, rue de la Doua, F-69100 Villeurbanne, France; abdoullatif.baraket@isa-lyon.fr (A.B.); selim.boudjaoui@isa-lyon.fr (S.B.); juan.gallardo-gonzalez@univ-lyon1.fr (J.G.); nadia.zine@univ-lyon1.fr (N.Z.); monique.sigaud@univ-lyon1.fr (M.S.); marie.hangouet@isa-lyon.fr (M.H.); abdelhamid.errachid-el-salhi@univ-lyon1.fr (A.E.)

[2] Centro Nacional de Microelectrónica (IMB-CSIC) Campus UAB, Bellaterra, 08193 Barcelona, Spain; albert.alcacer@imb-cnm.csic.es (A.A.); angelos.streklas@imb-cnm.csic.es (A.S.); joan.bausells@imb-cnm.csic.es (J.B.)

* Correspondence: abhisonu6487@gmail.com; Tel.: +33-627748805

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Abstract: Acetone in human breath has been regarded as the important disease marker of Heart failure (HF). Therefore, preliminary study has been carried out for the use chemical sensor based on Polyaniline doped with [3,3′-Co(1,2-C2B9H11)2]−1 anion (PANI/COSANE) for the detection and quantification of acetone in human breath. This chemical sensor was prepared by Galvano-statically growing a polymeric layer based on PANI/COSANE and PANI/Nitrate by electrochemical polymerization onto the two different interdigitated gold microelectrodes on a silicon chip surface using cyclic voltammetry. Measurement of change in conductance due to the presence of acetone in its vicinity at room temperature (20–25 °C) is performed in differential configuration mode using Lock-in amplifier. The developed acetone sensor has been calibrated under different acetone atmospheres using a Lock-in amplifier. This novel Acetone micro sensor showed good response, recovery, and stability for the detection of acetone in the range of 1 ppm–8 ppm.

Keywords: acetone; interdigitated; Lock-in amplifier; metallocarboranes; conducting polymer

1. Introduction

Heart failure (HF) is a staggering clinical and public health problem, related with significant mortality, morbidity, and healthcare expenditures, particularly for those aged ≥65 years. HF is considered as a major cause of human death according to the World Health Organization (WHO) [1]. Conditions including high blood pressure or heart defects can cause HF. Patients suffering from HF experience several effects, such as difficulty in breathing at rest or doing exercise, fast or irregular heartbeat. Co-morbidities, such as chronic obstructive pulmonary disease, frequently accompany HF, contributing to increased morbidity and mortality.

Now, existing methods of diagnosis for HF rely heavily on classical methods which are based on tests conducted in central laboratories that may take several hours or even days from when tests are ordered to when results are received [2]. To solve this problem, real time analysis of certain valuable biomarkers in the breath through a reliable biosensors can play an important role in the early diagnosis of the disease. Breath analysis is the powerful tool to detect various diseases by quantification of different biomarker.

Acetone being the important biomarker for the heart failure disease. The median exhaled acetone concentration for healthy person is between 0.65 ppm and for heart failure diabetic patient it is reported to be more than 1.80 ppm [3]. Real time monitoring of acetone can alleviate the risk in heart failure patient.

The aim of this work, is to develop fast, reliable, easy to handle and minituarized solid state gas sensor for acetone detection using Polyaniline doped with $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^{-1}$ anion (PANI/COSANE) based chemical sensor. This chemical sensor was prepared by Galvano-statically growing polymeric layer based on PANI/COSANE and PANI/Nitrate by electrochemical polymerization onto the two different interdigitated gold microelectrodes on a silicon chip surface using cyclic voltammetry. Measurement of change in conductance due to the presence of acetone in its vicinity at room temperature (20–25 °C) is performed in differential configuration mode using Lock-in amplifier. This strategy allowed to avoid any problems of drift in the measured signal with two identical transducers of which one is covered with PANI/COSANE conductive layer and other is covered with PANI/Nitrate conductive layer.

2. Materials and Methods

2.1. Preparation of Sensitive Layer of PANI/COSANE onto the Gold Microelectrode

Polyaniline doped with $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^{-1}$ anion was galvanostatically grown by electrochemical polymerization on interdigitated gold microelectrodes. The solution was made of 0.019 M of $Cs[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]$ and 0.1 M of aniline in acetonitrile with 1 wt% water. The electrochemical polymerization was performed by cyclic voltammetry by applying 10 potential sweep cycles between 0.5 V and 2.0 V at scan rate of 80 mV/s. After electrodeposition, the microelectrodes were rinsed with deionized water and dried under air flow.

2.2. Preparation of Sensitive Layer of PANI/NITRATE onto the Gold Microelectrode

Polyaniline doped with nitrate anion was galvanostatically grown by electrochemical polymerization on different interdigitated gold microelectrodes. The solution was made of 1 M HNO_3 and 0.1 M of aniline in water. The electrochemical polymerization was carried out by applying ten potential sweep cycles between 0 V and 0.95 V at scan rate of 100 mV/s [4]. After electrodeposition, the microelectrodes were rinsed with deionized water and dried under air flow.

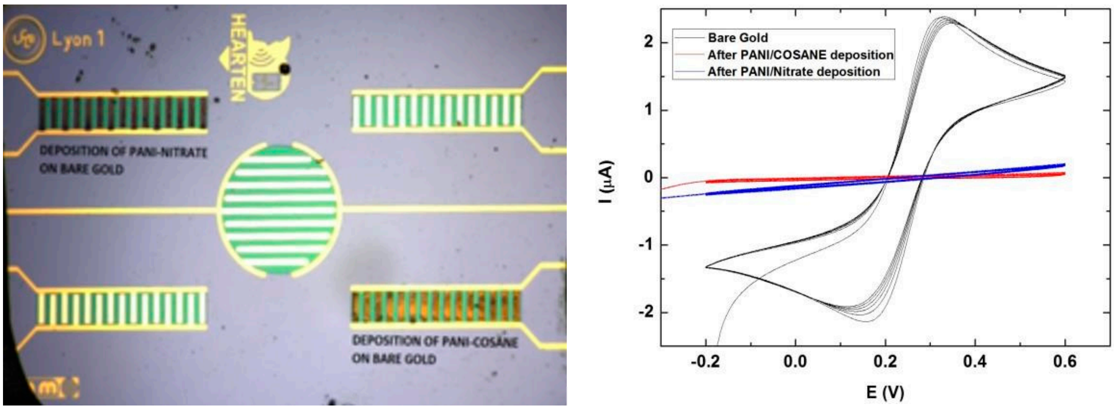
3. Results and Discussion

3.1. Electropolymerization

Electrochemical polymerization of aniline proceeds via a radical propagation mechanism and polyaniline (PANI) chain is formed by combinations of the two repeating units known as reduced benzoid units and oxidized quinoid units [5]. Owing to this, PANI has many unique properties and electronic conduction mechanisms that distinguish it from the rest of the conducting polymers [6]. For example the conductivity of PANI varies with the extent of oxidation (variation in the number of electrons) and the degree of protonation (variation in the number of protons).

Polyaniline doped with $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^{-1}$ anion was grown onto Gold substrate to form a thin selective membrane and the highly controlled deposition improved the mechanical and electrical contact between the polymeric membrane and the Gold surface. When PANI is oxidized after application of an anodic potential, the positive charges formed are localized in bipolaron states, stabilized by resonance in the conjugated polymer chain. The resulting polysemiquinone radical cation salt formed has conductivity on a semiconductor level [6].

Charge neutrality is achieved by the introduction of $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^{-1}$ anion or nitrate anion. Figure 1a and 1b show the interdigitated micro-electrode functionalized with PANI/COSANE and PANI/Nitrate and the cyclic voltammograms of Gold microelectrode, before and after electrochemical polymerization of PANI/COSANE and PANI/Nitrate solid and conductive layer. The former is used as the working micro-electrode since COSANE is highly selective towards acetone, while the latter is used as a reference.



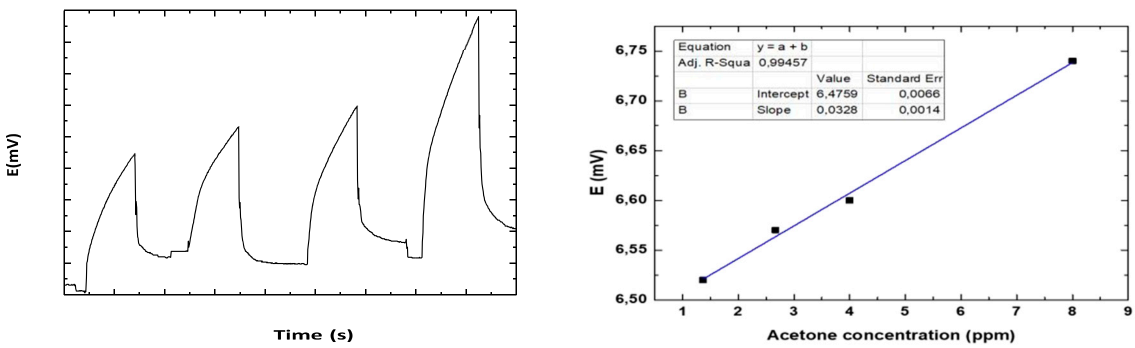
(**a**) (**b**)

Figure 1. Electrodeposition of PANI/COSANE and PANI/nitrate onto the interdigitated gold microelectrode: (**a**) Interdigitated microelectrode functionalized with PANI-COSANE and PANI-NITRATE; (**b**) Cyclic voltammetry result of bare gold in Fe(II)/Fe(III) cynide solution before and after electrodeposition of sensitive layer onto the Interdigitated micro-electrode.

3.2. Conductometric Measurement through Lock-in Amplifier

After the chemical sensor has been prepared, the performance of the sensor is tested using SR830 Lock-in Amplifier. Due to its phase sensitive detection, the Lock-in Amplifier can accurately measure even the small signals that are normally obscured by noise sources. Conductance is measured as shown in Figure 2a, by exposing the chemical sensor with known concentrations of acetone in humidified air in a gas cell.

In order to obtain, the best sensitivity of the chemical sensor, the electrical parameter of the Lock-in Amplifier has been optimized. Based on the optimized values, an AC voltage of 1 V and a reference frequency of 10 kHz are supplied to the two different Interdigitated Gold microelectrode which are connected in differential mode. The lock-in measured the voltage difference between the two microelectrode which are functionalized with conducting layer of PANI which are differently doped. Calibration curve is plotted and the linearity is checked in the range of 1 ppm to 8 ppm. It can be seen from the calibration curve as shown in Figure 2b that the sensor has a sensitivity of 0.0328 mV/ppm with a limit of detection of 1 ppm. The study also showed better selectivity and repeatability for this configuration towards acetone in comparison to ethanol and methanol. The results for the selectivity and repeatability can be presented under request.



(**a**) (**b**)

Figure 2. Measurement of change in Conductance in presence of Acetone in the gas surrounding the sensor using Lock-in amplifier: (**a**) Sensor response from lock in amplifier for acetone concentration

of 1.37 ppm, 2.67 ppm, 4.00 ppm and 8.00 ppm; (**b**) Calibration curve for PANI/COSANE based biosensor at various concentration of acetone.

3.3. Conclusions

In this preliminary work, the development of a solid state chemical sensor for detection of low concentration of acetone is reported. The gas sensor can work at room temperature with a high performance demonstrated by good, response, recovery, stability and repeatability. The developed chemical sensor has the big potential to be used for detection of acetone in human breath for the heart failure patient as it is trouble free, painless and non-invasive and has relatively fast response time.

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Conflicts of Interest: The author do not have any conflict of interest to be declared.

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