Organometallic Compounds for Gas and VOC Sensing

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ABSTRACT

With the recent advancement in artificial intelligence and machine learning (AI/ML), the electronic nose (e-Nose) technology has improved significantly in the last decade. However, relying on the signals produced by an array of gas and volatile organic compound (VOC) sensors used as the hardware of an e-Nose, the overall performance of the system is limited by the sensor types and sensing mechanisms. The majority of the commercially available gas/VOC sensors are using metal-oxide (MOX) thin films. Although MOX sensors are relatively stable, they are extremely power-hungry. Therefore, other materials have been investigated for gas and VOC sensing. In this work, we have focused on the application of organometallic compounds as a low-cost and low-power alternative to the MOX sensors. Copper Phthalocyanine (CuPc) has been tested in both forms of a chemiresistor and an electrochemical cell. In the electrochemical design, the material presented a unique selectivity to formic acid due to a protonation reaction. However, removing contaminants from the electrolyte of an electrochemical cell is challenging and limits the repeatability of the sensor response. In contrast, in a thin-film design (chemiresistor), CuPc responds to various VOCs including ethanol, isoproapanol, and acetone, but due to the lack of the protonation mechanism, the selectivity response was not observed. Our studies on ZnPc and CoPc, also, are promising for designing an array of metal phthalocyanines (MPcs) as the hardware of an e-Nose to address the shortcomings in the MOX technology.

Keywords: Chemiresistors, Gas sensing, Volatile Organic Compounds (VOCs), Metal Phthalocyanines (MPcs)

1. INTRODUCTION

Humans can identify and distinguish different odors through their olfactory sensing system. This capability allows us to enjoy the aroma of food/wine or assess the safety of the environment around us. However, the olfactory system in some animals is superior to that in humans through which they can detect more diverse viral chemicals at much lower concentrations. Particularly canine dogs have been trained by law enforcement agencies for the detection of drugs and explosive materials. Also, recent studies show that dogs can help in the detection of microbial growth in buildings [1]. The expenses related to training dogs, the limited information that can be communicated between a dog and a person, and endangering an animal for the detection of toxic or explosive substances have motivated scientists and engineers to design an electronic nose (e-nose) to be used for different applications. There are commercial sensors for the detection of certain gases and volatile organic compounds (VOCs) such as CO_2, H_2, ethanol, etc. Theoretically, an array of different sensors can be used to detect and measure the concentration of various chemicals in a mixed gas environment. However, due to the relatively poor selectivity of the existing sensors, the cross-response from different sensors requires a smart algorithm for data interpretation. In this regard, e-nose devices are essentially composed of a sensor array connected to a microcontroller and an artificial intelligence/machine learning (AI/ML) algorithm that processes the signals from the sensor array. The capabilities of different devices depend on the number of sensors, the sensor characteristics, the device algorithm, and the training cycles. With the advancement in AI/ML in recent years, it is feasible to process data at a high enough speed for real-time applications. Yet, sensors with higher sensitivity and selectivity can significantly improve the quality of e-nose devices.

The majority of existing e-nose devices use metal oxide (MOX) thin film technology as sensing materials. Nanostructures of MOXs such as ZnO, WO_3, and SnO_2 have been used widely in the form of resistors, diodes, and transistors for making sensors being used in e-nose devices [2-9]. The dangling bonds at the surface of the materials allow the oxygen atoms to be reactive to the adsorbed chemicals, consequently, changing their electrical properties [9]. However, as shown in Figure 1 (inset), their relatively poor selectivity is a serious shortcoming not being able to distinguish for example various alcohols. More importantly, as our experimental results show (Figure 1) [10], due to the required high temperature operation (200-400C), sensors are equipped with an internal heater that requires 20-30 min of warm-up time which limits the application of the sensors. In our research, we have studied the mechanism of odor receptors in the olfactory system to design room-temperature based sensors. As a result, two types of sensor modalities (electrochemical and chemiresistor) have been studied using metallophthalocyanine (MPc) compounds as sensing materials. Our results show the possibility of achieving high selectivity with an electrochemical design of the sensors.

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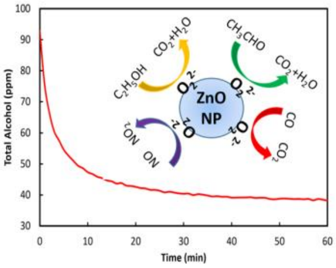

Figure 1. Warm-up cycle in MQ-3 MOX alcohol sensor [10]. (inset) Poor selectivity in MOXs (e.g. ZnO).

2. BACKGROUND

The neurons in the olfactory epithelium are equipped with odorant receptors (ORs) for detecting specific agents. ORs are essentially metalloproteins containing Cu^{2+}, Mn^{2+}, or Zn^{+} that are able to interact with the odorant molecules through redox reactions that generate electrochemical signals to the brain [11]. The head of ORs (including olfactory knobs and cilia) is buried under a thin layer of mucus (5-10 µm) that acts as the electrolyte. Odorants are first captured by the mucus and then conducted to the ORs [12]. To mimic the olfactory system, we designed an electrochemical sensor with synthetic chemoreceptors (MPcs) and a thin electrolyte layer. Earlier studies on MPcs and other organomettalic compounds have shown promising results when a thin solid film (non-electrochemical) was used in the form of a resistor being exposed to viral chemicals [13-15]. The detection-mechanism is based on the interaction between the odorant molecules and the central metal ions of the MPc structure (Zn^{+}, Cu^{2+}, Co^{2+}, etc.), which serve as Lewis acid by accepting electron pairs from the interacting molecule with the appropriate Lewis base characteristics [14, 16] which is similar to the mechanism in natural ORs [11]. Due to the high molecular stability in MPcs and based on our earlier results from four differnet MPcs [17], we are working towards an array of MPc-based sensors for developing an e-nose. In this work, we present the results from testing two types of sensors made with CuPc and other MPcs. The first type is a paper based electrochemical sensor with a thin layer of electrolyte to mimic the mucus layer over ORs. The second device structure is a simple chemiresistor that was fabricated on interdigitated electrodes with a thin solid film of MPc.

3. METHODOLOGY

3.1 Materials and equipment

Chemicals including CuPc, CoPc, ZnPc, multi-walled Carbon Nanotubes (CNTs), sodium dodecylbenzenesulfonate (SDBS), potassium chloride (KCl), $K_3[Fe(CN)_6]$, formic acid (HCOOH), and tetrahydrofuran (THF) were purchased from Sigma-Aldrich. Acetone, ethanol, and isopropanol were purchased from Alfa-Aesar. An 1800 W probe sonicator (model: FB-1800N) was used for making a homogeneous CNT solution. For baking the CNT-coated paper electrodes, a Fisher Scientific model 280 isotemp lab vacuum furnace (120 V 550 W) was used. The measurements were conducted by a VersaSTAT 4 potentiostat/galvanostat in a two-electrode experimental setup. A custom-made setup was used for controlling the flow of gases into the chamber where the sample was located.

3.2 Electrode fabrication and electrolyte preparation

Paper based electrodes were made by applying multi-walled CNT ink on printing paper. We followed our recipe in [17] for synthesizing CNT ink in which 300 mg CNT and 150 mg SDBS were added in 30 mL deionized water and the solution was sonicated for 35 minutes at 35 W power and 40 J energy. 1 ml of synthesized ink was applied on a piece of paper (4 cm x 7 cm). The coated paper was heated in a vacuum furnace at 120 °C for 30 min. To achieve conductive enough electrodes, the process was repeated three times. For the electrochemical device fabrication, 4 cm x 1.5 cm strips were cut out from the CNT coated papers. A CNT coated strip was saved as the counter electrode. For making the working electrode, another strip was coated with 30 µL of CuPc solution (2 mg CuPc in 1 ml of tetrahydrofuran, THF). To make an electrochemical cell, we made 0.1 mM solution of $K_3[Fe(CN)_6]$/KCl electrolyte by mixing 0.066 g $K_3[Fe(CN)_6]$ and 0.1 M KCl in 200 mL deionized water. The chemiresistors were made by drop casting of 80 µl of CuPc/ 150 µl of CoPc/ 140 µl of ZnPc (2 mg of MPc in 1 ml of THF) on three different commercially available interdigitated gold electrodes built on polyethylene terephthalate (PET) substrate (purchased from amazon). The electrodes are 1 cm x 1cm with 15 fingers at each side with the line width of 100 µm and spacing between the fingers of 50 µm.

3.3 Test setup

As shown in Figure 2.a, a sensor device was assembled by placing a blank piece of paper (9 cm x 3 cm) between the counter and the working electrode as the separator. The separator was bent to form an upside-down U-shape structure with the legs touching a reservoir containing the electrolyte. To hold all pieces together a 3D printed structure was designed and used (not shown in the figure). In this configuration, the separator gets wet when being in contact with the electrolyte, and via the capillary force both the working and counter electrodes become wet as well with the electrolyte bridging between the two electrodes. The sensor was placed in a chamber that was connected to the gas and VOC setup in the lab (Figure 2.b and c). Controlling the flow of the compressed air through the tubes containing VOCs the response of the sensor was recorded via a potentiostat connected to the electrodes. For the thin-film sensors, solutions of CuPc, CoPc, and ZnPc were drop cast on the commercially available interdigitated gold electrodes.

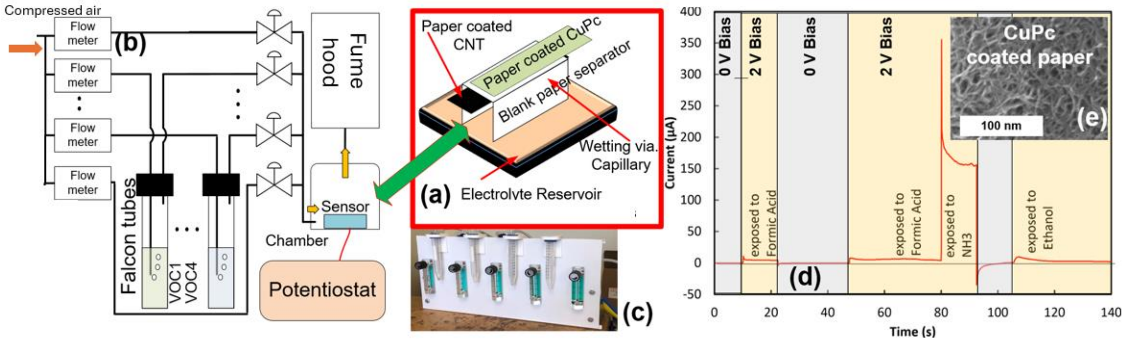

Figure 2. (a) Schematic of the sensor with paper-based electrodes and electrolyte. (b) Schematic & (c) image of the setup for testing the sensors with different VOCs/gases. (d) Chronoamperometry results of a CuPc sensor. (e) SEM image of the electrode.

4. RESULTS and DISCUSSION

The scanning electron microscopy image of the CuPc (Figure 2.e) coated paper shows a uniform coating with the diffused CuPc into the fiber structure of the paper. First the sensor was tested by applying a constant voltage of 2.0 V between the working and counter electrode when it was exposed to various VOCs. As Figure 2.d shows, the response to ammonia was much stronger than the response to formic acid or ethanol. A series of experiments were conducted where a constant voltage of 2.0 V was applied to the device for 5 min to achieve the baseline current, I_s. Then using the gas system, the sensor was exposed to various VOCs and the current at the steady state level has been recorded as I_g. The response of the sensor has been calculated using the equation below with the estimated concentration of the exposed VOC:

$$\boldsymbol{Response} = \frac{\boldsymbol{I_g - I_s}}{\boldsymbol{concentration}} \quad (1)$$

Figure 3.a and b show sample data from measurement in response to methanol and formic acid at the concentrations of 800 ppm and 200 ppm, respectively. While the baseline reached ~1.5 mA level at the steady state level, when the sample was exposed to methanol, the current was reduced to 0.6 mA. In contrast, the current showed an increase of 0.28 mA after exposure to formic acid. Figure 3.c summarizes the response of the electrochemical sensor to a few VOCs. The results clearly show a distinguishable selectivity of the sensor toward formic acid with a positive change in the current (reduction in the sensor resistance) with a negative response to other tested VOCs (increase in the resistance). In that combination, acetic acid presents a weak neutral response.

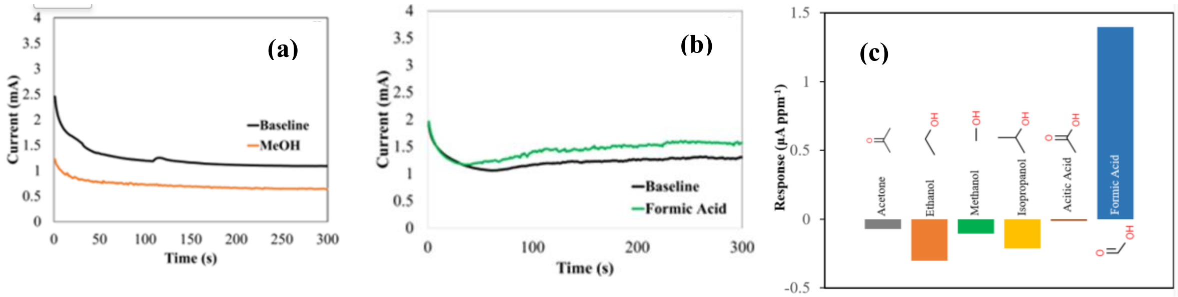

Figure 3. the chronoamperometry results from the electrochemical sensor to (a) methanol and (b) formic acid. (c) the summary of the response of the CuPc based electrochemical sensor to a few VOCs.

The fact that the response to some VOCs results in increasing the resistance of the cell while formic acid causes a reduction of resistance implies that there are two mechanisms of interaction between CuPc and the VOCs. Previous studies suggest that alcohols and ketones can interact with CuPc through Lewis acid-base interactions [13, 15]. In this mechanism, the empty orbital of the metal ion in the MPc is behaving like a Lewis acid and the paired orbital in N, O, or S of the VOC acts as a Lewis base [16]. But formic acid can protonate the nitrogen atom in the MPc structure. This type of interaction apparently reduced the resistance of the CuPc presenting a strong increase in the sensor current. While further studies are needed to understand better the mechanism of interactions, the sensor results clearly show the selective response of MPc. However, for practical applications, there are some concerns in using electrochemical design. A major concern is repeatability. Due to the liquid media standing between the viral molecules and the sensitive materials on the electrode (i.e., CuPc), once VOC molecules are captured through the electrolyte, naturally they are trapped. Hence, stopping the exposure of the sensor to the VOC does not show a reversible process and the sensor must be disposed of. It should be mentioned that in biology systems, there is a natural mechanism disposing of mucus from the olfactory epithelium. The fresh layer of mucus produced by Bowman glands rejuvenates the sensing system.

In the lack of a mechanism for rejuvenation in our electrochemical system, we studied the application of CuPcs and two other MPcs (CoPc and ZnPc) in a solid-state form. To fabricate the thin film sensors 80 µl of the CuPc solution was drop casted on the commercially purchased interdigitated gold electrodes (Figure 4.a inset). After drying, the sensor was loaded into the testing chamber. The potentiostat was programmed to apply constant current to the sensor and monitor the voltage (galvanostatic mode). The results of measured resistance from three different chemiresistors (CuPc, CoPC, and ZnPc) when being exposed to three different VOCs (ethanol, isopropanol and acetone) each at three different concentrations are presented in Figure 4. Among the sensors, the resistance of the sensors before exposure to any VOC was 6.26 MΩ for CuPc, 223 MΩ for CoPc, and 4.88 MΩ for ZnPc. The results clearly show that CuPc and CoPc respond to the exposed chemicals, but ZnPc does not show any correlation with the type of the chemicals and their concentrations. Both CuPc and CoPc have responded to the chemicals and recovered after stopping the exposure. It should be noted that no heat was applied to the sensors during the recovery cycles. Comparing CuPc and CoPc, the strong response to isopropanol in CuPc is notable. Considering the electrochemical response from CuPc for ethanol, isopropanol, and acetone suggests that the presence of the liquid interface in the electrochemical cell has a significant impact on how CuPc responded to the VOCs. The results of the experiments encourage further exploration of chemiresistors using various MPcs.

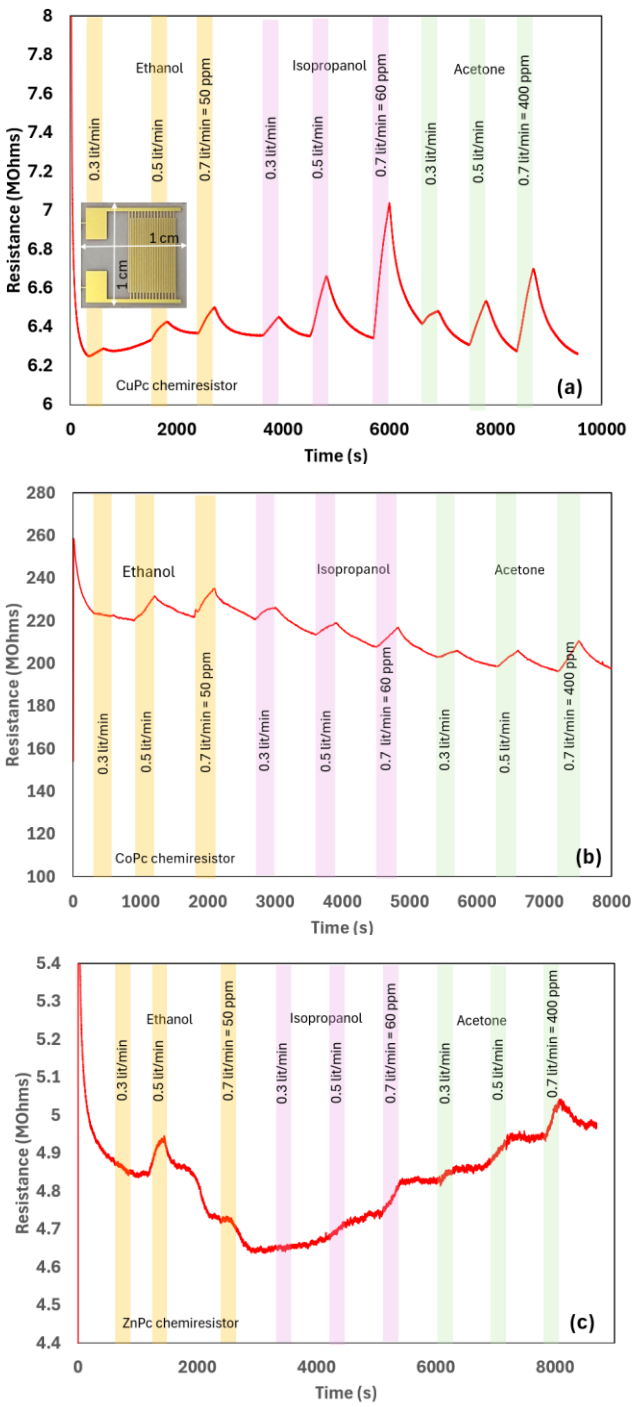

Figure 4. The resistance changes of the chemiresistors made from solid thin film of (a) CuPc, (b) CoPc, and (c) ZnPc to ethanol, isopropanol, and acetone at three different concentrations. The flow rate of the air bubbled through the VOC tubes have been set for 0.3 l/min, 0.5 l/min and 0.7 l/min for each VOC. The equivalent of the ppm for the 0.7 l/min has been marked for each VOC. (inset) A picture of the commercially purchased interdigitated gold electrode.

5. CONCLUSION

Our results clearly show the potential of using MPcs as VOC sensors to be operated at room temperature without any requirement for internal heating. The electrochemical design presented a unique selectivity to formic acid due to the feasibility of protonation of the Pc molecule. However, the electrochemical sensor could not be used without any proper rejuvenation process. In contrast, the chemiresistor design has a reliable and repeatable response. Using MPcs with different metal ion cores has shown different responses to the tested VOCs encouraging the use of an array of MPcs for building an electronic nose in the future.

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