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Functionalized Copper Phthalocyanine and Zinc Phthalocyanine as a Coating Layer on the Sensitivity of QCM-Based VOCs Sensor

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ABSTRACT

The sensitivity of a QCM-based VOCs sensor with two kinds of a metal phthalocyanine, i.e., copper phthalocyanine (CuPc) and zinc phthalocyanine (ZnPc), was examined for various VOCs. The sensitivity of the two metal phthalocyanine was determined by the compatibility of the overlapped metal orbitals (Cu(II) dan Zn(II)) and the corresponding VOCs. The CuPc and the ZnPc layer were deposited on the quartz crystal oscillator by a vacuum evaporation method. The frequency shift and the sensitivity of the sensors with the two functional layers were tested using 5 VOCs: formaldehyde, propanol, ethanol, toluene, and ketone. The CuPc sensor showed the highest sensitivity to formaldehyde. On the other hand, the ZnPc was highly sensitive to ethanol.

Keywords: QCM; metal phthalocyanine; sensitivity; metal orbital; VOCs.

INTRODUCTION

Currently, different detection principles or sensor types have already been developed to sense formaldehyde gas, such as chromatography[1], resistance sensor[2], the colorimetric principle[3,4], and QCM (quartz crystal microbalance)[5,6]. However, the most problems with the current sensors and methods are the portable or handheld size, linearity, range, and other essential parameters. Among all the above sensors, QCM has received intensive attention in the gas sensing method because of its good performances, such as range, selectivity, and sensitivity [7,8]. QCM also works at low temperatures and is easily modified [9]. Regarding range parameters, another advantage of QCM is the ability to measure nanogram-scale changes in mass. The mass changes caused by gas molecules adsorbed on the electrodes are proportional to frequency shifts based on the Sauerbrey equation [10].

The biggest problem of QCM is that bare QCM electrodes (such as silver) hardly respond to gas molecules [11]. This central problem has to be overcome by modifying the QCM surface with various sensitive materials such as composite[5], graphene oxide[12,13], and metal oxides[14]. Among all, copper phthalocyanine (CuPc) and zinc phthalocyanine (ZnPc) have the potential to be developed as gaseous sensors[15–17]. It is related to phthalocyanine (Pc), which is among the most functional molecular materials due to its interesting electrical and optical properties [15,18–20].

The Copper Phthalocyanine (CuPc) and zinc phthalocyanine (ZnPc) are functional materials with the respective molecular formulas $CuC_{32}H_{16}N_8$ and $ZnC_{32}H_{16}N_8$ with the hybrid orbital being d^2sp^3 with 17 electrons for CuPc and 19 electrons for ZnPc. CuPc and ZnPC have

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been applied as gas sensors because of the sensitive nature of these materials [15,20]. This property of sensitive nature is contributed by the π-π* interactions between CuPc or ZnPc atoms and the atoms present in the gas. All these bonds are dominated by van der Waals bonds which the phthalocyanine group contributes. The bonds include hydrogen bonds and ion-dipole bonds.

Cupc and ZnPc sensors detect analyte gas by sorption (adsorption and absorption). Some researchers study the adsorption of gases with MPCs due to the π-π* interactions between CuPc or ZnPc atoms and the atoms present in the gas[15, 21]. On the other hand, Collins[21] studied the interaction between the ZnPc layer and NH_3 gas which formed the NH_3-ZnPc complex, by observing the hybridization process of ZnPc with NH_3 gas. The behavior of Znpc was studied by considering the tendency of the divalent ion (Zn(II)) to form a tetrahedral configuration using a $4s4p^3$ hybrid. In the Znpc molecule, the planar shape of the ZnPc macrocycle ring does not allow outer orbital complexes to form using $4s4p^24d$ hybridization. This work focuses on a monolayer CuPc and ZnPc thin film on the Ag surface of a bare QCM. CuPc and ZnPc were used as the sensitive coating material deposited on the surface of QCM. This study aims to develop a novel formaldehyde sensor with high performance related to airborne VOC detection in low-range concentrations. In this research, the interaction between Cu(II) and Zn(II) with VOC gas was studied through the tendency of outer orbitals to form using hybridization.

METHODS

Sensors

Three QCM sensors were used as the gas sensors (diameter = 8.7 mm, electrode area (A) = 0.196 cm^2). These sensors were purchased from PT. Great Microtama, Indonesia. They were Q1, Q2, and Q3. Q1 was a bare QCM with a baseline frequency of 5 MHz. Q2 and Q3 were coated QCM with sensitive films: CuPc (Q2) and ZnPc (Q3), using the evaporation method (purity = 99%, deposition time = 5 minutes, annealing temperature = 220°C).

Gas Samples

This study used five different gasses: ethanol, toluene, propanol, formaldehyde, and acetone, obtained from the aeration process. All gasses were purchased on the local market around Malang city, Indonesia (standard solutions). Each gas was varied into four different concentrations (as the measured concentrations, C_m): C_1 (70 mg/L), C_2 (80 mg/L), C_3 (90 mg/L), and C_4 (100 mg/L) inside gas chambers to identify the sensor performances under different exposure concentrations (Figure. 1).

Experimental Setup

The experimental setup was conducted inside an experimental chamber. All sensors (Q1, Q2, and Q3) were placed inside a sensor box (volume $V = 0.028\ m^3$). The sensor electrodes were connected to the frequency counter device to count the frequency shift (Δf) due to the gas exposure (Figure. 1)[13]. Then, the first gas, ethanol with a concentration of C_1, was exposed to the sensor box for 180 s. This measurement was repeated three times to get the best value. All treatments were also applied for all gas types and gas concentrations.

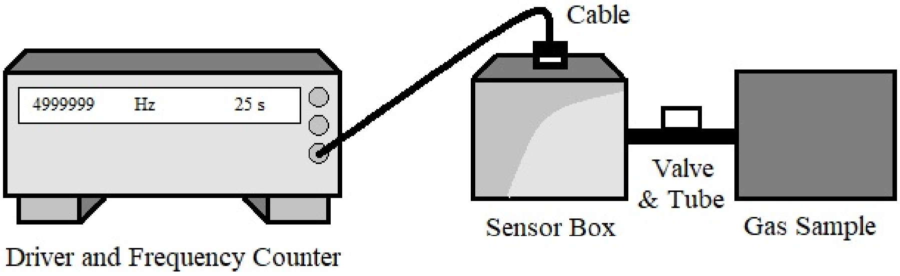

Figure 1. The experimental setup for the performance analysis.

Sensor Performance Evaluation

The sensor's performances were identified as accuracy, linearity (interpreted as the regression coefficient R^2), sensitivity (S), and selectivity. Related to the Sauerbrey equation (Eq. 1), Δf is linear to the deposited gas mass (Δm) on the QCM's surface [10]. The calculated concentrations (C_c) from Q1, Q2, and Q3 were calculated using the equations:

$$\Delta m = -\frac{\Delta f \,.\, A \,.\, \sqrt{\rho\,\mu}}{2f_o^2} \tag{1}$$

$$C_c = \frac{\Delta m}{V} \tag{2}$$

Constants μ and ρ are shear modulus (2.947 x 10^{11} g/cm.s^2) and crystal density (2.684 g/cm^3), respectively. The measured (C_m) and calculated concentrations (C_c) were used to determine the sensor performance, including sensitivity (S), selectivity, and linearity (R^2) parameters [16].

$$S = -\frac{\Delta f}{C_m} \tag{3}$$

RESULTS AND DISCUSSION

Frequency Responses

Ethanol measurements show interesting results (Figure 2). Q1, the bare QCM sensor, has the tiniest frequency shift. This sensor does not have a good frequency response related to ethanol gas exposure. The maximum frequency responses are obtained from C_3 and C_4, with frequency shifts >340 Hz. Q2 provides good results with the saturated zone. All resulting frequency shifts indicate that the frequencies do not return to their baseline points. It can be assumed that CuPc gets no recovery times since the frequency shifts below 0 Hz for all measurement times. The maximum frequency is referred to as C_4, with a value of 18,000 Hz. In Q3, the maximum frequency shifts are >350,000 Hz. Q3 also recovers well for all dose concentrations (having a good recovery and reversibility), C_1-C_4. These results confirm the ability of Q3 to sense volatile ethanol gas with the highest frequency shift.

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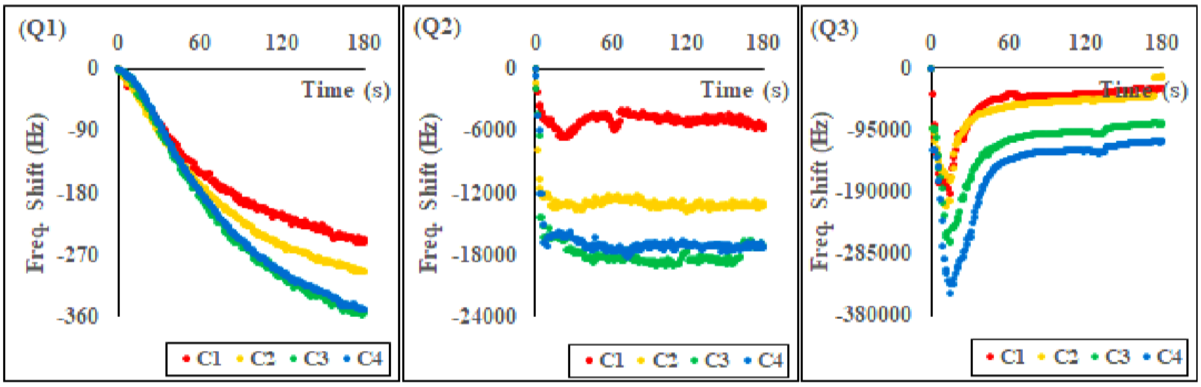

Figure 2. The frequency shifts of QCM sensors for ethanol gas measurements.

Figure 3 shows the frequency responses under toluene gas exposures. The figure shows that Q1 results do not reach 480 Hz of the measured frequency shift. These values are so small than those in Q2. The CuPc-coated sensor performs better than Q1, resulting in a higher frequency shift. The maximum frequency shift is detected from C4, >16,000 Hz. Q1 and Q2 values represent the saturated conditions since the frequency responses do not return to their baseline points, 0 Hz. These two sensors also have similar response patterns. In Q3, the maximum frequency shift is > 50,000 Hz. Compared to Q1 and Q2, Q3 has the best frequency shift to detect toluene gas. Despite the best frequency obtained from Q3, Q3 still has no recovery stage.

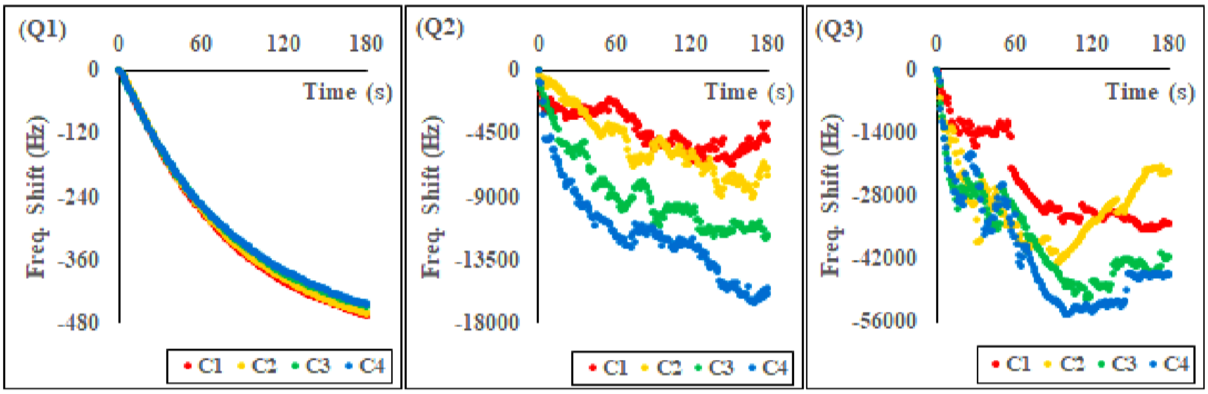

Figure 3. The frequency shifts of QCM sensors for toluene gas measurements.

Figure 4 interprets the frequency responses of Q1-Q3 using propanol gas. These gas measurements indicate there is no recovery stage for all dose concentrations. Similar to Q1, Q2 does not indicate the recovery stage since all frequencies do not return to their baselines (showing saturated conditions). However, the frequency shifts are better than Q1, indicated by higher frequency shifts. In Q1, the maximum frequency shift is only -417 Hz, resulting in C4 as the most dose concentration.

All results show that Q3 is the best sensing element for propanol detection among Q1 and Q2 (in terms of their frequencies). However, there is no significant difference between Q2 and Q3. Interestingly, the propanol measurement using a ZnPc-coated sensor shows the recovery stage, in which the maximum frequencies return to their baselines.

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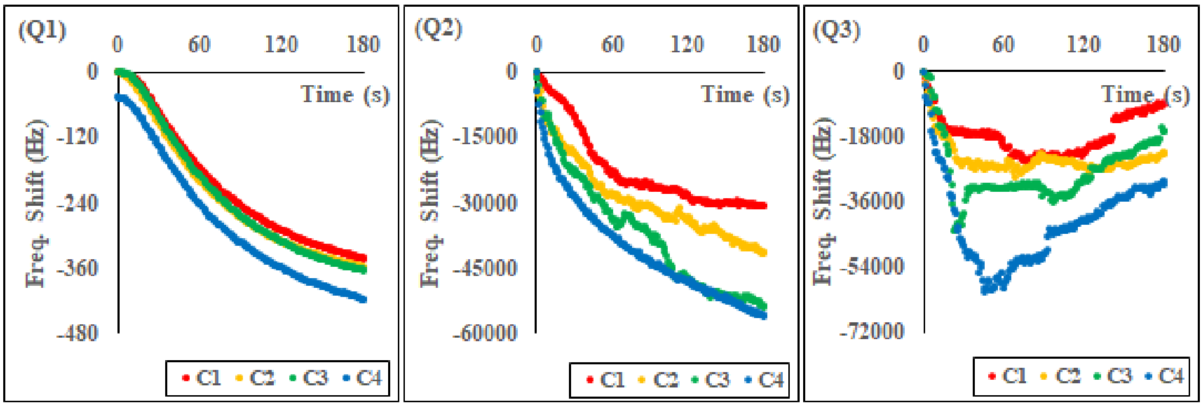

Figure 4. The frequency shifts of QCM sensors for propanol gas measurements.

Acetone measurement results (Figure 5) in Q2 show that the frequencies of C_1-C_4 reach the maximum values. Then, the frequencies increase and return to their fundamental frequency. This condition means the acetone volatile gas measurements do not show maximum or saturation since all frequencies are similar to their baseline conditions. Different results are obtained in Q3. The Q3 sensor does not show consistent results. Despite having good frequency shifts (up to 100,000 Hz), this sensor has many interchanges, indicating poor reversibility, recovery, and stability. As expected for Q1 or the bare sensor, this sensor only has 0 Hz to 339 Hz of the frequency shifts for acetone measurement. These values confirm that Q1 does not perform well in detecting or sensing acetone gas since the frequency shifts are too low.

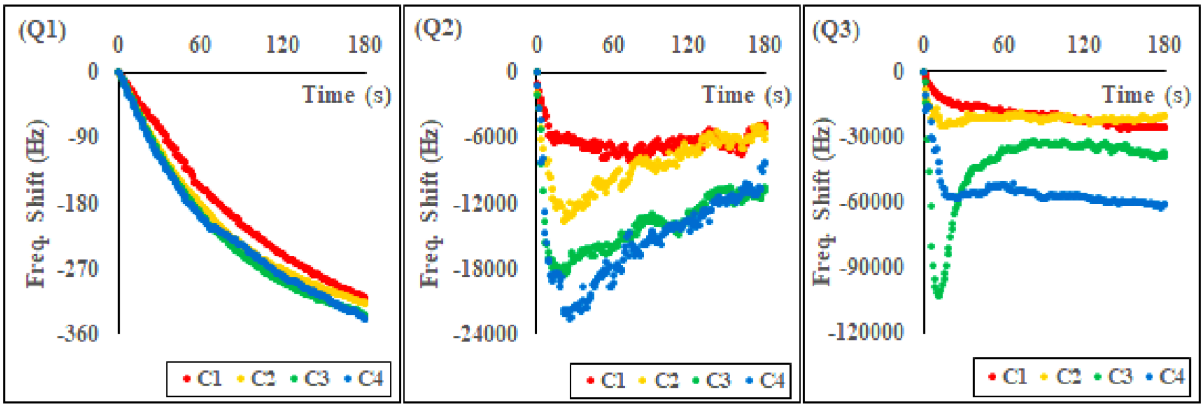

Figure 5. The frequency shifts of QCM sensors for acetone gas measurements.

Formaldehyde measurements have different trendlines for Q1, Q2, and Q3. As seen in Figure 6, CuPc coated-sensor (Q2) shows that the final frequencies do not return to their baseline frequencies. From the initial measurement time, Q2 has 0 Hz of frequency shift since these values are still constant (fundamental frequency). Then, the frequency shifts decrease several times until the values reach the saturated zone. All concentrations, C1, C2, C3, and C4 show these trendlines. Similar cases are found in Q3. Q3 data shows that all concentration variations do not return to their baseline. The graph shows that C_1 (red dots) has the least frequency shifts, while C_4 (blue dots) gets the most. In Q1, the most frequency shift is obtained from C_4 (blue dots), -11 Hz. Like the other sensors, the frequencies do not return to the baseline. All these results confirm that all sensors have no good recovery performance in detecting formaldehyde gas. In other words, volatile formaldehyde gas may influence the QCM's reversibility.

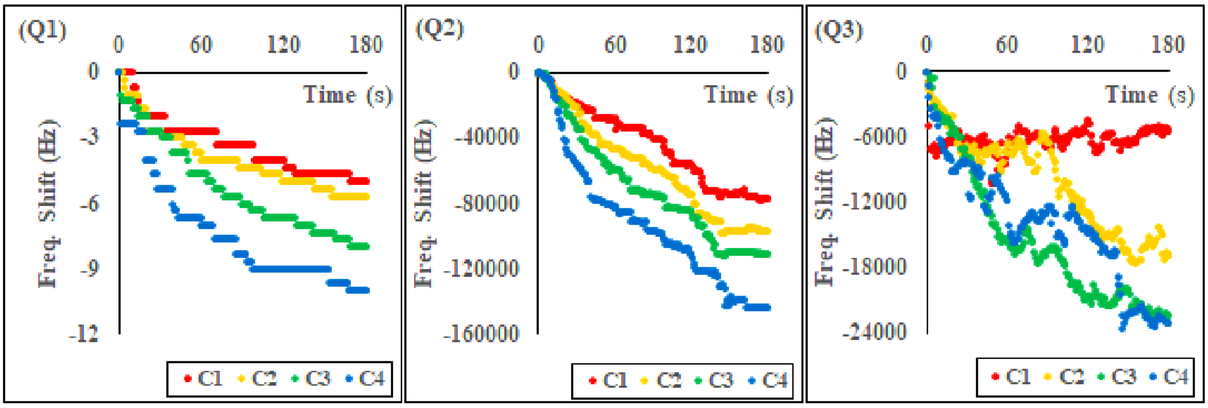

Figure 6. The frequency shifts of QCM sensors for formaldehyde gas measurements.

Sensitivity and Selectivity

The sensor's characteristic is identified by the selectivity and sensitivity levels (Figure 7a-e). As seen in Figure 7a, propanol measurement using Q1 (bare QCM, grey bars) has only 4-5 Hz.L/mg of the sensitivity level. This value is low compared to Q2 (CuPc, orange bars) since Q2 has a sensitivity level of 448-605 Hz.L/mg. In this gas test, Q3 (ZnPc, blue bars) has similar values to Q2, with sensitivity levels of 389-618 Hz.L/mg. Both Q2 and Q3 have similar performances. These results assume that the coated sensors (Q2 and Q3) are more sensitive than the bare sensor in propanol gas sensing.

In Figure 7b, Q3 (ZnPc) sensor has a sensitivity of 351-1,119 Hz.L/mg for the 1st – 4th acetone concentrations. Q3 has better sensitivity levels than Q1 and Q2. A bare QCM has only 3-4 Hz.L/mg, a very low response. Q2 has higher sensitivity levels than Q1, with values of 143 Hz.L/mg (C_1), 183 Hz.L/mg (C_2), 218 Hz.L/mg (C_3), and 239 Hz.L/mg (C_4). In other words, acetone gas is more detected in Q3 than in Q1 and Q2. Figure 7c shows the QCM's sensitivity to the toluene gas with different gas concentrations. The bare QCM (Q1) exhibits the smallest sensitivity levels. This sensor only has 4-7 Hz.Liter/mg of the sensitivity levels for C_1-C_4. Better results are obtained from Q2, with 122-168 Hz values.Liter/mg. Then, the best sensitivity for toluene sensing is shown by Q3 as the highest sensitivity level of toluene gas sensing. This sensor has a sensitivity of 550-729 Hz.L/mg.

In formaldehyde gas measurement (Figure 7d), Q1-Q3 have different sensitivity levels in all concentration variations. The bare QCM has no sensitivity for the formaldehyde measurement since the sensitivity level is 0 Hz.L/mg. The average sensitivity levels of Q2 (CuPc) and Q3 (ZnPc) are 1,274 Hz.L/mg and 237 Hz.L/mg, respectively, for Q2 and Q3. These average sensitivities show that CuPc coated-QCM has the most sensitivity levels for formaldehyde sensing, with calculated sensitivities of 1,124 Hz.L/mg (C_1), 1,239 Hz.L/mg (C_2), 1,270 Hz.L/mg (C_3), and 1,465 Hz.Liter/mg (C_4). Compared to acetone, toluene, and propanol measurements, Q2 has the most sensitive characteristics in formaldehyde gas (selective to formaldehyde gas).

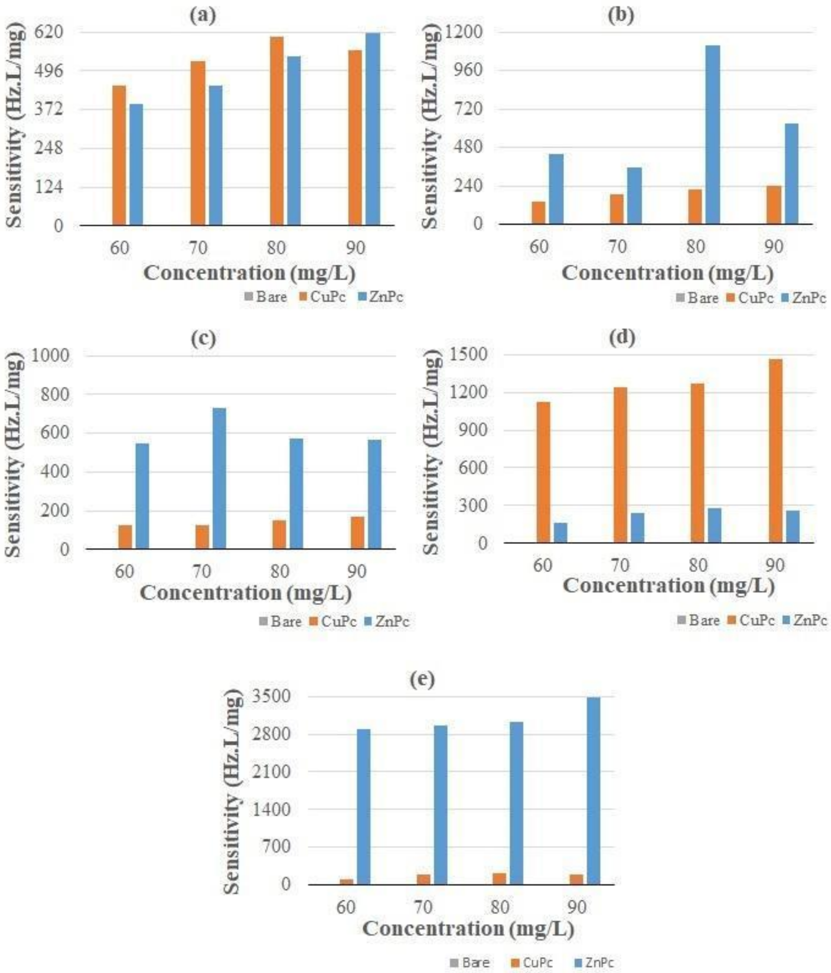

Figure 7. The sensitivity levels of Q1 (bare QCM), Q2 (CuPc coated-QCM), and Q3 (ZnPc coated-QCM) sensors for different gasses: (a) propanol; (b) acetone; (c) toluene; (d) formaldehyde; and (e) ethanol.

The last gas measurement results, ethanol, are interpreted in Figure 7e. As expected, the bare sensor (grey bars) has minor sensitivity to ethanol, with sensitivity levels of 4 Hz.L/mg. The CuPc coated-QCM (orange bars) results in better results, resulting in 104 Hz.L/mg, 195 Hz.L/mg, 218 Hz.L/mg, and 189 Hz.L/mg, respectively, for C_1, C_2, C_3, and C_4. Interestingly, Q3 has the most sensitive performance to ethanol gas (blue bars). This ZnPc coated-QCM shows the highest sensitivity levels among Q1 and Q2 (2,901 Hz.L/mg to 3,477 Hz.L/mg). The difference between Q2 and Q3 is more than 2,700 Hz.L/mg indicates a significant selectivity of ZnPc coated-QCM to ethanol gas.

Linearity and Accuracy

Linearity performance is indicated by the R^2 value of the resulting trendline, calculated from the comparison between measured (x-axis) and calculated (y-axis) concentrations.

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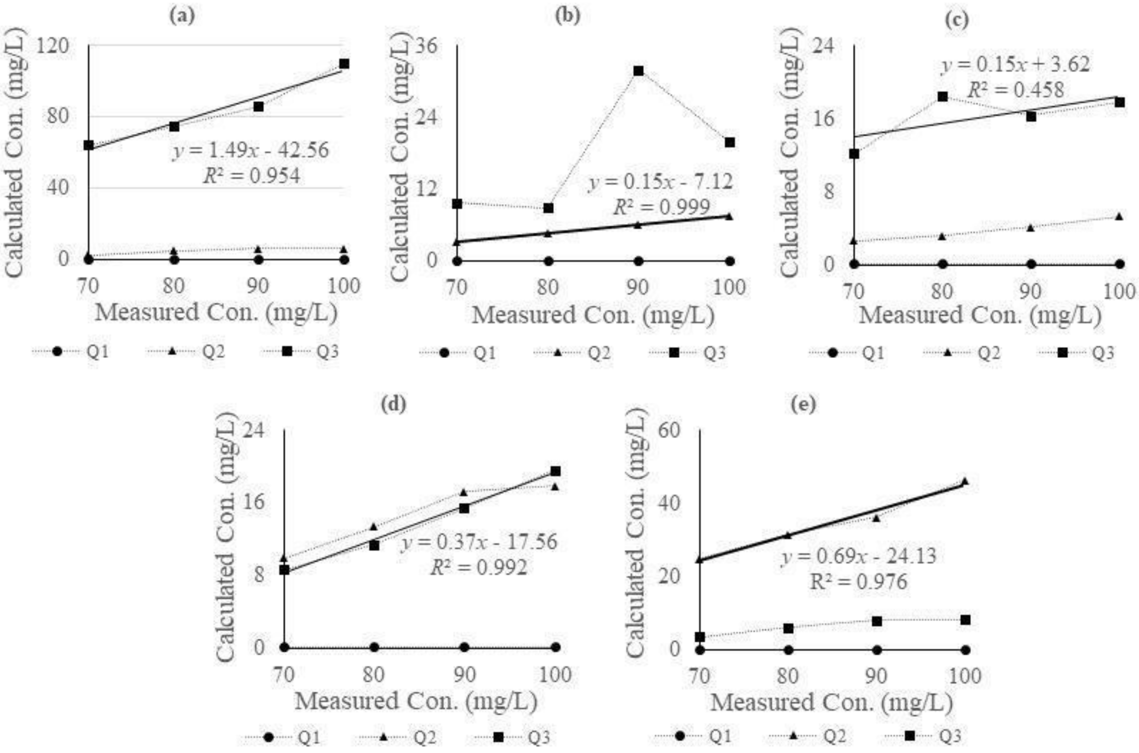

Figure 8. The linearity levels of Q1 (bare QCM), Q2 (CuPc coated-QCM), and Q3 (ZnPc coated-QCM) sensors for different gasses: (a) ethanol; (b) acetone; (c) toluene; (d) propanol; and (e) formaldehyde.

The R^2 value shows how linear the data is and how good the accuracy is. These characteristics are interpreted in Figure 8. As seen in Figure 8a, the comparison between measured and calculated ethanol concentrations of Q3 has good linearity (R^2 = 0.954) and accuracy (93%). The accuracy can be identified by the increase in both calculated and measured ethanol concentrations. The calculated concentration also decreases when the measured one decreases. In contrast, Q1 (R^2 = 0.836) and Q2 (R^2 = 0.791) have lower calculated concentrations than the measured concentration. The calculated ethanol gas concentrations at Q1 and Q2 do not approach the accurate concentration (measured concentration). Different results are obtained at acetone comparison. Despite providing good R^2 values, this gas does not represent good linearity for Q1 (0.965), Q2 (0.999), and Q3 (0.415). The calculated acetone concentrations are very low (below the threshold, low accuracy of 0-20%, Figure 8b). Similar results are obtained at toluene (Figure 8c), showing low toluene concentrations for Q1 – Q3. The best comparison in Q3 with the regression coefficient R^2 = 0.458 (accuracy = 19%). The other two QCMs do not represent accurate results (calculated concentrations are only 0-18 mg/L). In Figure 8d, the highest calculated concentrations are only 18 mg/L (Q2) and 20 mg/L (Q3), while the actual concentration is 100 mg/L (accuracy < 18%). The best regression coefficient is 0.992, obtained from Q3. For the last gas, formaldehyde, the best result is interpreted by Q2 (CuPc-coated QCM sensor). This sensor has better accuracy (40%) and linearity (R^2 = 0.976) than Q1 (accuracy = 0%) and Q3 (accuracy = 8%). In other words, Q2 performs best in formaldehyde gas, while Q3 performs well in ethanol gas. Q1 does not show good accuracy for all gas.

Discussions

CuPc coating has the highest selectivity and sensitivity to formaldehyde, followed by propanol, acetone, and ethanol, and the lowest sensitivity to toluene. In contrast, the ZnPc layer

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had the highest sensitivity to ethanol, followed by acetone, toluene, and propanol, and the least sensitivity to formaldehyde. Several factors that may affect the selectivity and sensitivity are the size of the analyte molecule (VOC) as indicated by the molecular weight value, the solubility parameter between the VOC and the coating (Hansen Solubility Parameter), and the similarity of the chemical structure of the VOC to the layer. The chemical structures of CuPc and ZnPc (Figure 8) and VOC gas (Ethanol, Acetone, Propanol Formaldehyde Toluene are shown in Figure 9.

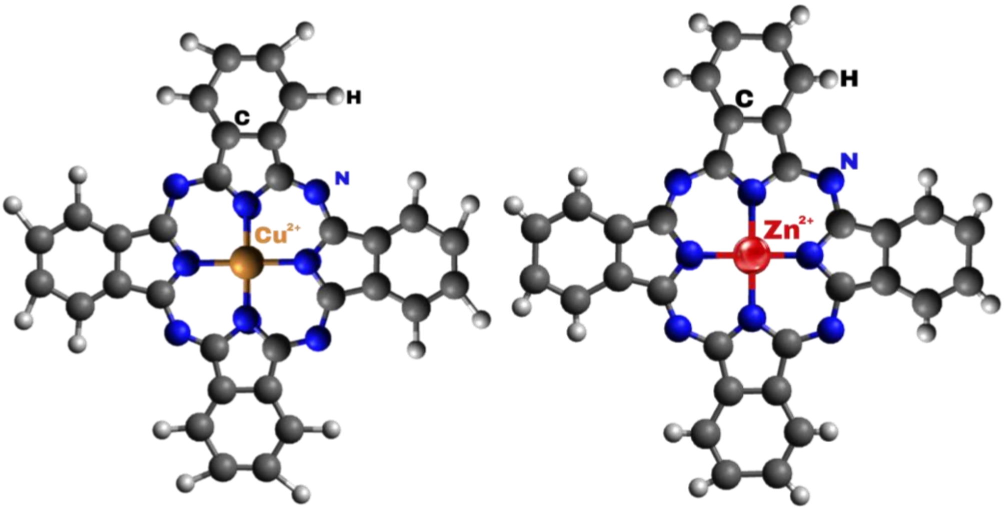

Figure 8. The chemical structure of copper phthalocyanine and zinc phthalocyanine

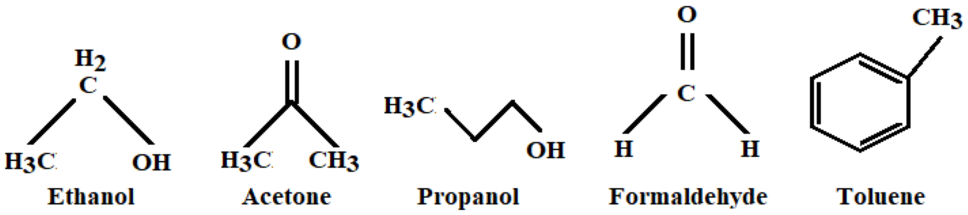

Figure 9. The chemical structure of various VOCs (ethanol, acetone, propanol, formaldehyde, and toluene) used for the response with CuPc and ZnPc layer on the QCM sensor.

The difference in reactivity between Cu(II) and Zn(II) lies in the number of electrons in the 3d orbitals. In Cu(II), the 3d orbital is filled with 9 electrons; in Zn(II), the 3d orbital is filled with 10 electrons. Cu(II) and Zn(II) bind to phthalocyanine using d^2sp^3 hybridization so that in Cu(II), the hybridization is filled with 17 electrons, while in Zn(II), it is filled with 18 or completely. The Cu(II) phthalocyanine and formaldehyde engage well due to the 2p electrons of the formaldehyde oxygen interacting with the 3d orbitals of Cu(II), which are filled with 9 electrons and form additional π bonds. The interaction between formaldehyde and Zn(II) is not reinforced because the 3d orbitals are complete, and d^2sp^3 hybridization has a maximum of 18 electrons. The density of free electrons in the formaldehyde oxygen atom is close to the nucleus because the s character in sp^2 hybridization is 33%, while in ethanol, oxygen atoms with sp^3 hybridization are 25%, as shown in Figure 10. Thus, the interaction between ethanol and metal is better without the additional interaction. The exchange of ketones with the two phthalocyanine metals is hindered by the increased methyl groups preventing the oxygen atoms from moving closer to the metals. That is why, in this study, ZnPc has 237 Hz.L/mg of the sensitivity level for formaldehyde gas which is higher than the bare QCM sensor (0 Hz.L/mg).

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However, CuPc coated-QCM is the best sensor for formaldehyde sensing with the best sensitivity level, 1,274 Hz.L/mg. Then, the best interaction for the ethanol gas is obtained at Q3 or ZnPc coated-QCM sensor. In this case, ZnPc coated-QCM shows the highest sensitivity levels among Q1 and Q2.

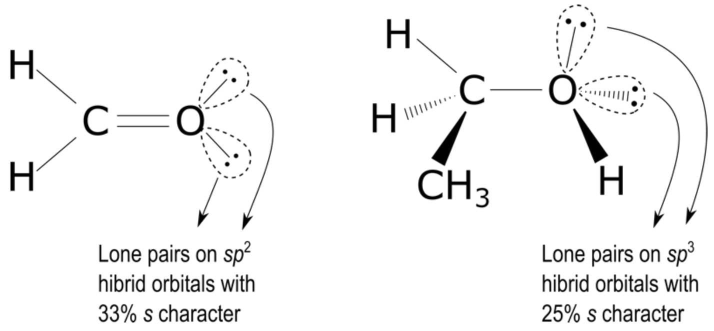

Figure 10. The schematic diagram of Sp2 and Sp3 hybrid orbitals of the metal (Cu(II) dan Zn(II)), which allow the metal to bind the VOCs

CONCLUSION

According to the results, it can be concluded that a bare quartz crystal microbalance (Q1) has no specific performance indicated by the low sensitivity, selectivity, and linearity levels. The selectivity and sensitivity levels are influenced by the chemical structure of the volatile gasses and the reactivity between Cu(II) dan Zn(II) orbital. The coated sensors perform better, resulting in a higher frequency shift than the bare sensor. Q2 (CuPc layer) has the best response in formaldehyde gas sensing. Q3 (ZnPc layer) performs better in ethanol gas testing.

CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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