(https://www.news.com.au/national/western-australia/police-dog-sniffs-out-140000-at-perth-airport/news-story/13ffc58c6b64ac0cf15369727ee7dbd5)

Detecting Odor Molecules Using Metal Quantum Dot

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ABSTRACT

This research was designed to develop an odor sensor that detects gas molecules based on the resistance change of a cobalt-doped graphene layer. Applying crystal field theory to the cobalt-graphene system, the resistance of the system will increase as an odorant comes closer. In addition, the energy gap created by the odorant will differ for each type of odorant. Thus, if the coordination power of odor molecules causes different energy gaps with cobalt, then different odor molecules in mixtures of gas can be differentiated in the detection. In order to detect mixture gases, detecting individual odorant with different binding power must be tested with the change of resistance. The most change was demonstrated by the highest concentration with 72.0% of acetone, and the resistance increased by 5.763 MΩ. Although this result proves the hypothesis successfully, further investigation for the variety of gas must be followed in order to develop a practical electronic nose that detects various smell molecules from mixture gases.

INTRODUCTION

In many airports and other important places, there are sniffing dogs for the detection of hazardous materials such as drugs and bombs. Even though they are very convenient, because they are dealing with dangerous material, the dogs are exposed to great danger that can cause fatal injury. For this reason, an electronic nose should be created that can detect certain material without any human or living things involving.

Scientists nowadays in various field are studying about senses of human and trying to mimic them. So, various studies and industrial applications are led by scientists around the globe. However, it is true that olfactory is the least known system and applicable system due to its complexity.

(https://psicologiaunam2018.blogspot.com/)

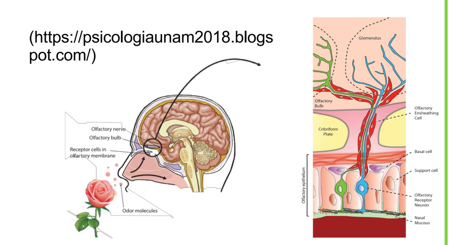


Figure 1. Olfactory system of human nose

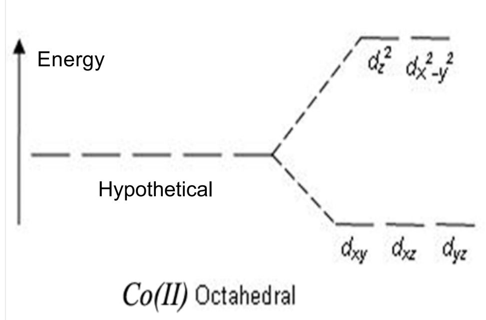
The most recent research trend involving electronic nose studies is leading towards about the application such as a medical application of previously developed electronic nose rather than developing a new method of the electronic nose. One of the traditional gas sensors is Metal Oxide Semiconductor Gas Sensor (MOS). It uses a semiconductor that interacts with the gas outside of the semiconductor and uses the change in conductivity (Fine, 2010). However, such electronic nose has restrictions such as some requires high temperature and has restriction on the type of gas that it can detect.

In this research, Crystal Field Theory of metal quantum dot is used in order to detect odorant measuring the change of time depended resistance.

Orbitals, Crystal Field Theory

The ligand (odorant in this experiment) is slightly negatively changed and metal is positively charged. So, they are attracted to each other.

Because the ligand has slightly negative charged, they repel each other. Thus, the odorant comes closer to the metal with octahedral shape, keeping certain distance from each other. As the ligand comes closer to the metal, because each d-orbital of the metal points in different way, the energy created by repelling with odorant will differ from each other, making a split of energy. (See figure 3)



(https://www.chegg.com/homework-help/questions-and-answers/sketch-crystal-field-d-orbital-splitting-diagrams-chromium-iii-cobalt-ii-)

Figure 2. Crystal field theory – Splitting of energy level of Co(II)

The energy gap created between bonding level and the conductive band (anti-bonding) will make the resistance of the metal to increase since electron needs more energy to go on to the conductive band from bonding level. In this experiment Cobalt(II) is used as the metal.

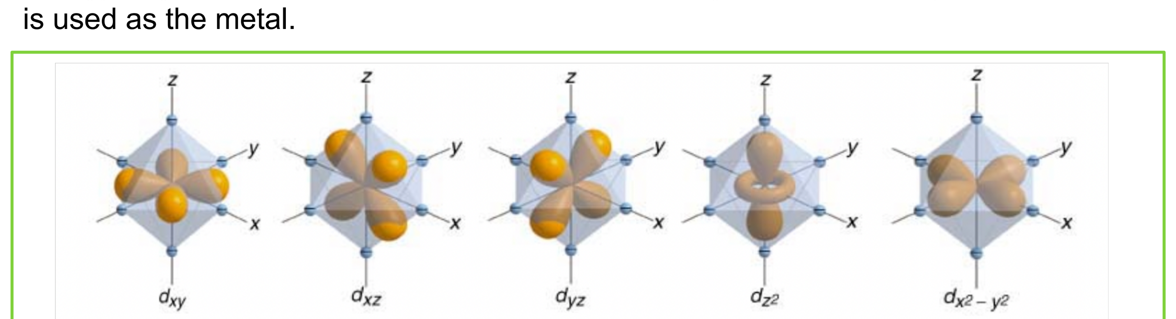


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Figure 3. Crystal Field Theory: Diagram of d-orbital and the ligand in octahedral shape

Polarity

Graphene is a layer of carbon that is structured in honeycomb structure. So, electronegativity of atoms is same, making graphene non-polar molecule.

The odorant, acetone and acetonitrile are polar molecules, having acetone more polar then acetonitrile. The negative end of acetone is in oxygen and nitrogen in acetonitrile.

For the cobalt has slightly positive charge, the odor molecule which is partially negative, will be attracted to the cobalt, making the detection.

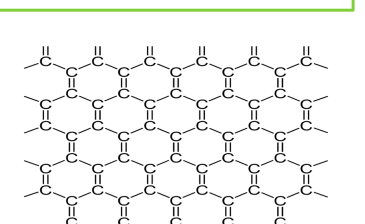


Figure 4. Atomic structure of graphene

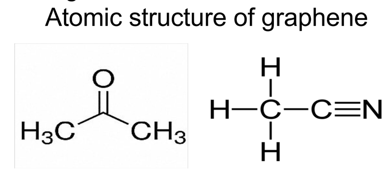


Figure 5. Atomic structure

PURPOSE

The purpose of this research is to develop odor sensor that detects gas molecules based on the resistance change over time of the cobalt-doped graphene layer. An electronic nose that detects various smell molecules from mixture gases will be created.

Hypothesis If the coordination power of odor molecules causes different energy gaps with different heavy metals, then different odor molecules in mixtures can be differentiated in detection using time depended resistance.

METHOD

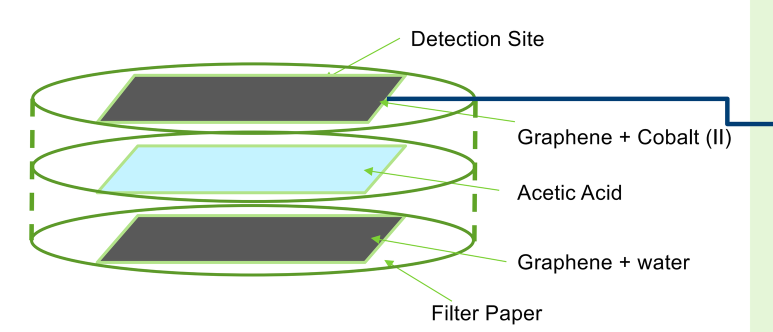


Figure 6. Structure of Gas Sensor

In this experiment, graphene is mixed with cobalt nitrate, and it is painted on one layer of filter paper, and graphene with water on another layer of filter paper. Between two layers, a layer with acetic acid is placed. This will act as a connection between two sites (Figure 6). Acetone or Acetonitrile will be in the air in different concentration in each trials. Once the odorant attaches to the detection site with cobalt, each cobalt's d-orbital's energy will change according to the orbital's position as described in crystal field theory. The energy gap created by the ligand (odorant) will make the energy gap between the conduction band and bonding level will go up as well as the resistance of the layer.

Because only one side of the sensor has cobalt, that side will be slightly positive (low potential energy for valence band initially). Thus, the odor molecule which is slightly negative will be more attracted to that side, making the differences between two sides of the sensor. This is connected to a 2 probe multimeter to measure the changes.

Gas Sensor-Detailed

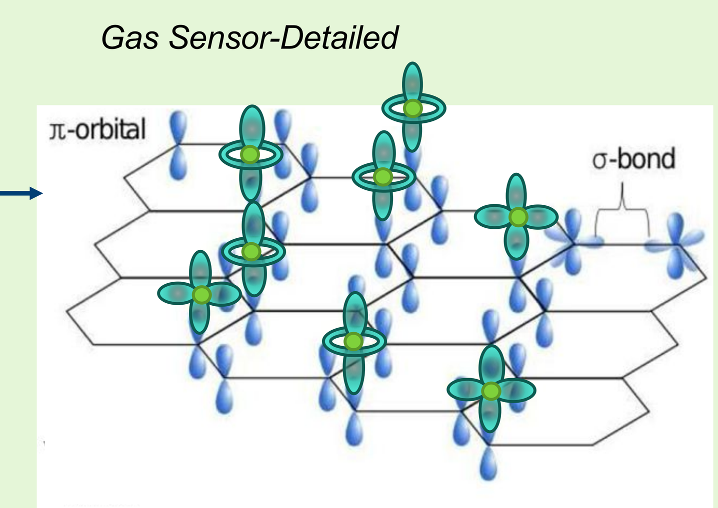


Figure 7. Drawing of pi-bonding of graphene doped with d-orbital of cobalt

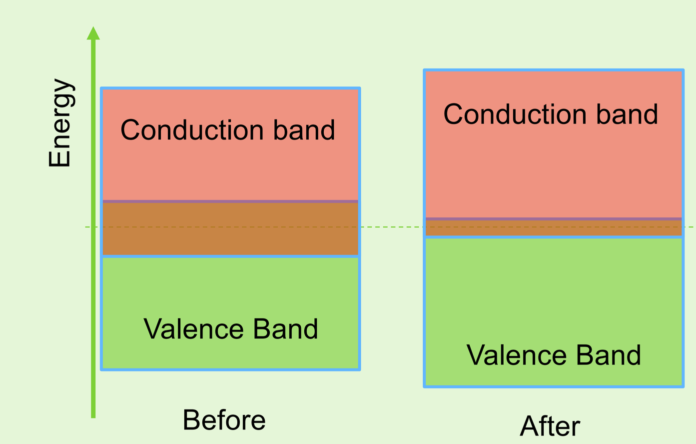


Figure 8. Drawing of conduction band and the valence band before and after the coordination of ligand.

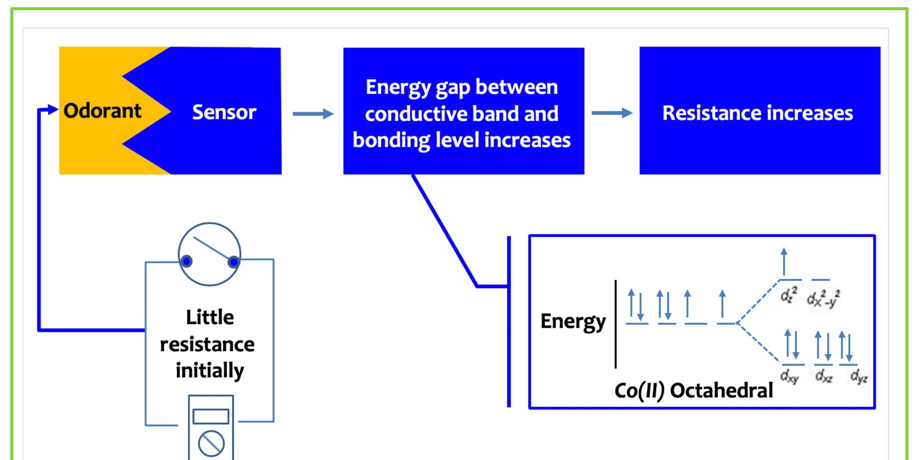


Figure 9. Flow chart of the method used in the experiment

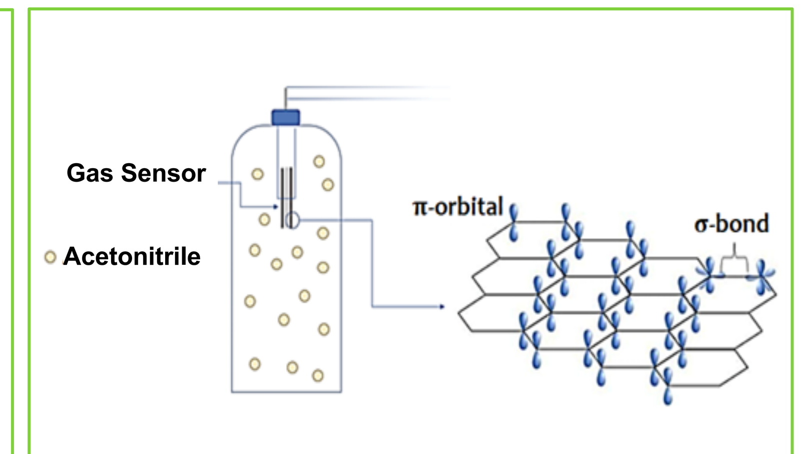
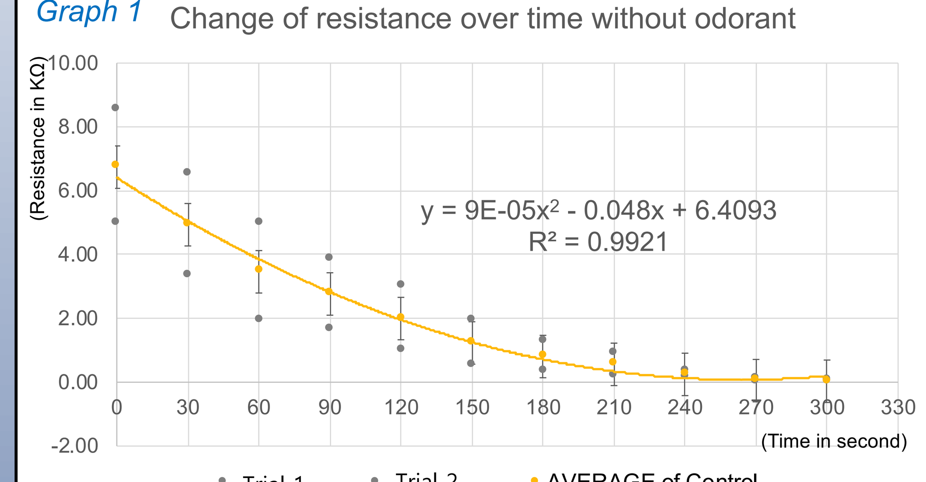


Figure 10. Drawing of how the experiment is done

The source of error can cause by the leakage of odorant from the flask during the trial.

RESULTS

Graph 1 Change of resistance over time without odorant



Insight 1

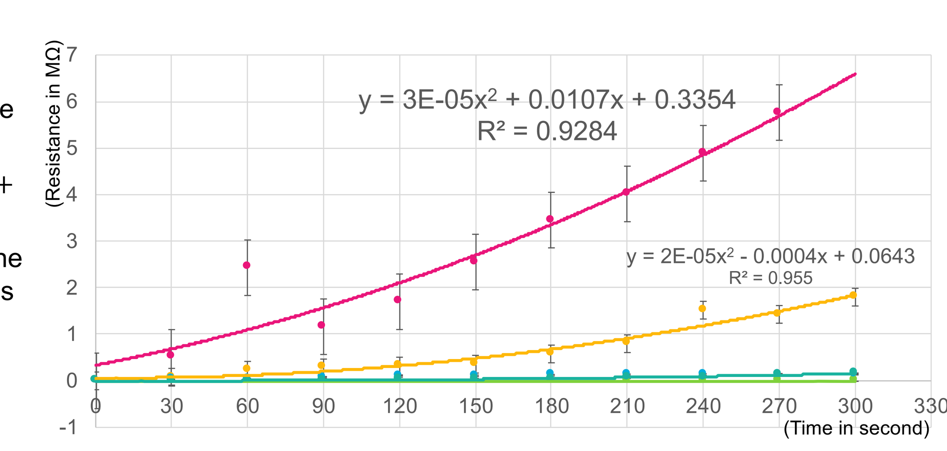
- **Unit** = KΩ
- **Odorant**= None
- **Explanation**:

The best fit of the average of the control group is $y = 9 * 10^{-5}x^2 - 0.048x + 6.4093$

Because r^2 is 0.99, the quadratic equation fits this data well.

Thus, the resistance decreased in quadratic from. This indicates that without odorant, the resistance decreases.

Graph 2 Change in resistance over time with different concentrations of Acetone



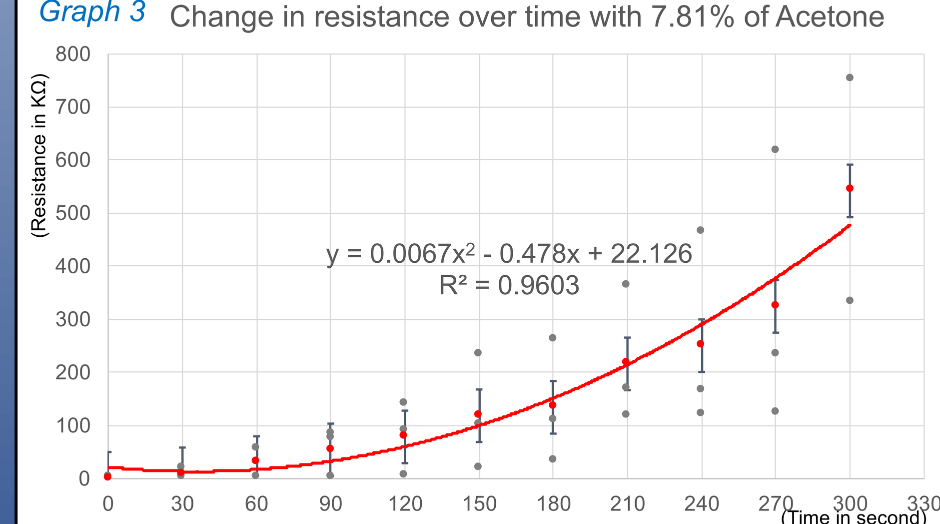
Insight 2

- **Unit** = MΩ
- **Odorant**= Acetone (C_3H_6O)
- **Explanation**:

The resistance went up rapidly as the concentration of acetone increases.

The overall trend of each trial: The change of resistance is a quadratic increase. This indicates that if there are higher concentration of odorant, more ligand binds to Cobalt, making the resistance increase rapidly.

Graph 3 Change in resistance over time with 7.81% of Acetone



Insight 3

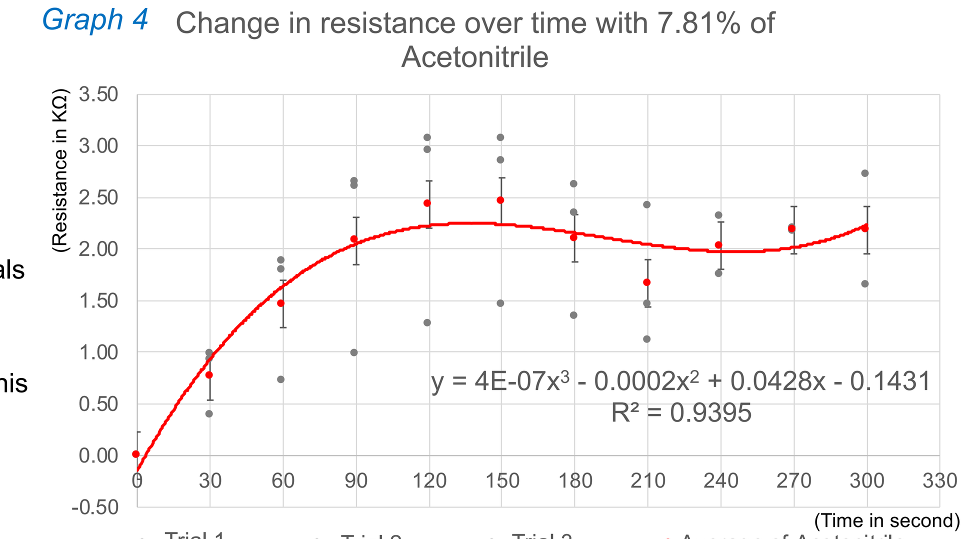
- **Unit** = KΩ
- **Odorant**: 7.81% of Acetone (C_3H_6O)
- **Explanation**:

The best fit equation of the average of these trials is $y = 0.0067x^2 - 0.478x + 22.126$

Because r^2 is 0.96, the quadratic equation fits this data well.

Thus, the resistance increased in quadratic from.

Graph 4 Change in resistance over time with 7.81% of Acetonitrile



Insight 4

- **Unit** = KΩ
- **Odorant**: Acetonitrile (C_2H_3N)
- **Explanation:**

The best fit equation of the average of these trials is

$y = 4 * 10^{-7}x^3 - 0.0002x^2 + 0.0428x - 0.1431.$

The graph increased rapidly in first 2-3 minutes. However, it started to decrease or level out after 3 minutes.

DISCUSSION

Because the acetic acid in the middle layer can evaporate while doing the experiment, the initial resistance can be different from each trial. However, the change in resistance shows the same changes in the same group.

As the slightly negatively charged odorant comes closer to the cobalt, the energy gap between anti-bonding and bonding orbitals increases according to the orbital's position. Looking at graph 2, 3, and 4, it shows that the resistance goes up, indicating that the odorant is attached to the detection site.

The most ideal graph is an exponential function that increases rapidly in the beginning and starts to level out as time goes. As shown in graph 4, the resistance goes up rapidly until 2 to 3 minutes and started to level out or decrease a little for the sensor with 7.81% of acetonitrile. This indicates that odorant was attaching to the sensor until 2-3 minutes and stopped.

The result also showed that the rate of change (the slope of the graph) increases as the concentration of the odorant increase. Looking graph 2, the trial with higher concentration showed rapid change than the trial with lower concentration. This indicates that if there are higher concentration of odorant, more ligand binds to Cobalt, making the resistance increase rapidly.

Comparing graph 3 and 4, because the change in resistance with acetone is greater than with acetonitrile, it can be concluded that acetone has the higher ability to bind with cobalt, and easily detected. However, because graph 3 didn't show the full ideal graph that levels out within the 300 seconds, it can also be concluded that the reaction in acetone was slower than acetonitrile in graph 3 that showed the full curve. The probable reason for the acetone has higher changes than acetonitrile is that acetone has higher volatility than acetonitrile and that ligand power of acetone is slightly higher than acetonitrile.

CONCLUSIONS

This electronic nose is able to differentiate the gases by looking at the trend, and the concentration by looking at the rate of change. Therefore, there is a potential for this method for detecting various odorant molecules.

Going forward, Artificial Intelligence is very provisional, powerful and useful technology. Machine learning which is a part of AI, analyze senses such as picture for vision and voice for hearing. However, application of olfactory system is yet inadequate compared to other senses (Kim). Since this electronic nose converts the smell signal into visible electronic signal, it can contribute to the field of AI.

FUTURE WORK

In the future, tests on various heavy metals on various odorant in order to find the different trends of different odorants should be done in order to construct more practical electronic nose.

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