Detecting Odor Molecule 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.

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Introduction

In many airports and other important places, there are x-ray scanning machine and a sniffing dog for the detection of hazardous materials such as drugs and bombs. The detection dogs are very accurate and convenient; therefore, they are widely used. However, the dog can be in dangerous situations when detecting drugs or bombs. An electronic nose that can detect hazardous materials could significantly reduce the risk to dogs and humans.

Scientists nowadays in various field are studying about senses of human and trying to mimic them in the flow of technological advancement. So, a lot of parts of human senses are now almost discovered, and the technology of such senses are developed based on the founding. Furthermore, various studies and industrial applications such as computer senses are led by scientists around the globe. However, it is true that olfactory is the least known and least applicable system due to its complexity. Dr. Park stated, “although many studies on olfaction have been performed, an understanding of olfactory receptor has progressed slowly due to the lack of appropriate heterologous systems for expressing and assaying odorant responses” (Lee and Park 2010).

The most recent research trend about 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. (Dragonieri, Pennazza, Carratu, and Resta, 2017).

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, MOS sensors need relatively high temperature to sense the odorant. Thus, it is rather hard to applicate in real life.

Another developed gas sensor is the Bioelectronic nose. “Bioelectronic nose is based on naturally optimized molecular recognition of odorants with high sensitivity and selectivity” (Lee and Park 2010). With the database of different expression of the biological sensing element in the bioelectronic nose, the nose is able to identify the odorant. However, the limit of this bioelectronic nose is that it depends on living cells or protein to detect the odorant. Thus, the cost of producing the sensor is high. Also, it is not able to identify the odorant and the concentration at the same time.

Considering such limitation of such developed electronic noses, an electronic nose that can identify the odorant and calculate the concentration in a common condition is needed.

In this research, metal quantum dots act as the detection component. Quantum dot is a nanometer-sized crystal, usually based on metallic or on semiconductor materials, and cobalt (II) is used as the metal. Because of their reduced size, quantum dots have more attractive and sensitive properties than a bulk solid (Drbohlavova, 2009). Thus, it gets more effected by the changes of its surroundings. Having more surface area and such properties contribute to the sensitivity of the gas sensor. In order to make quantum dots, controlling the acidity and evaporation was done when making the sensor. The conduction band and valence band are created with the series of the quantum dot.

This detection of the odorant was measured by the change of resistance over time according to crystal field theory of the metal quantum dot. The crystal field theory states that as the ligand come closer a metal, the resistance increases due to the splitting of energy level. The ligand (odorant in this experiment) is partially, slightly negatively charged and metal is positively charged. So, they are attracted to each other.

However, the ligands 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 (Figgis 2002). (See figure 1 and 2)

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.

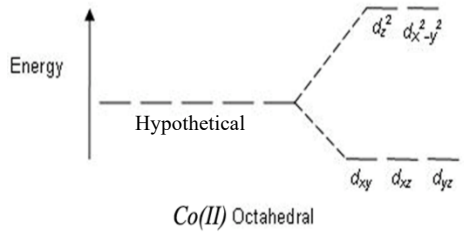

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Figure 1. Crystal field theory of Co(II)

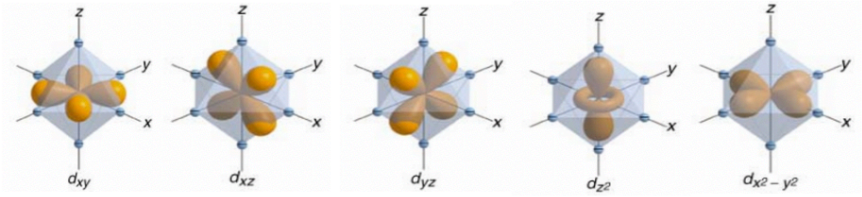

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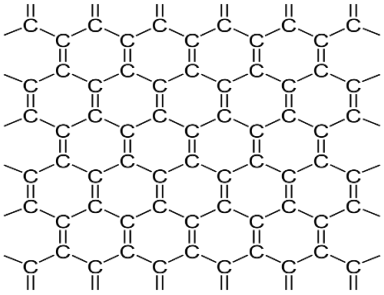
Figure 2. Crystal field theory: Diagram of d-orbital and the ligand in octahedral shape

Graphene is a layer of only carbon that is structured in honeycomb structure. So, electronegativity of atom is same, making electrons not to be attracted to certain place. Because no part of the molecule is relatively positive nor negative, graphene is non-polar molecule.

On the other hand, Acetonitrile and Acetone, the molecules that is tested in this experiment are polar, and having acetone having more polarity than acetonitrile. For the cobalt has slightly positive charge, the negative end of odor molecules will be attracted to the cobalt.



(http://graphenewholesale.com/graphene-structure)

Figure 3. Atomic structure of graphene

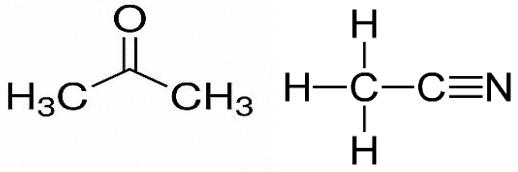


Figure 4. Atomic structure of acetone (left) and acetonitrile (right)

The purpose of this research is to develop odor sensors that detect gas molecules based on the resistance change of the cobalt-doped graphene layer, and furthermore, to develop an electronic nose that detects various smell molecules from mixture gases in the future. This experiment initiates the overall purpose of the research by using cobalt as the metal of detection and acetone and acetonitrile as the odorant.

This research will contribute to the scientific development of gas sensor by proposing a new method for gas sensors that would overcome the previously suggested problems of traditional gas sensors. In this electronic nose field, the electronic nose that is based on the crystal field theory is not very common, and this theory is almost new to this field.

Material and Method

The material that is needed for this research is: cobalt nitrate, acetone, acetonitrile, acetic acid, filter paper, water, and powder graphene.

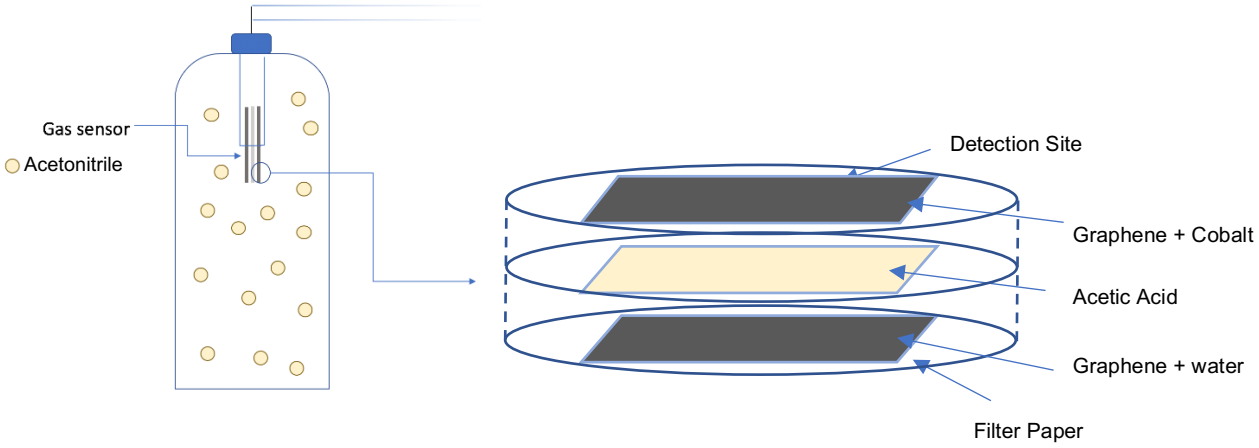


Figure 5. Structure of gas sensor

In order to make the electronic nose, graphene was mixed with cobalt nitrate, and it was 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 was placed. This acted as an electrical connection between two sites, as well as controlling pH of the sensor to make metal quantum dots (See Figure 5). Acetone or acetonitrile was in the air in different concentration. Once the odorant attached to the detection site with cobalt, each cobalt's d-orbital's energy changed according to

the orbital's position as described in crystal field theory, making changes in resistance of the nose.

Because only one side of the sensor had cobalt, that side was slightly positive (low potential energy for valence band initially). Thus, the odor molecule which was slightly negative was more attracted to that side, making the differences between two sides of the sensor.

In order to record the change in resistance of the electronic nose, a two-probe multimeter was connected to two graphene layers, and time dependent resistance was measured between two layers of graphene every 30 seconds until 5 minutes starting after the resistance stopped fluctuating in the beginning.

To see if this method works, high concentration such as 63.0% and 72.0% of acetone was tested. Then, the smaller concentration such as 1.67% and 7.81% was tested in order to see how precise and sensitive this was.

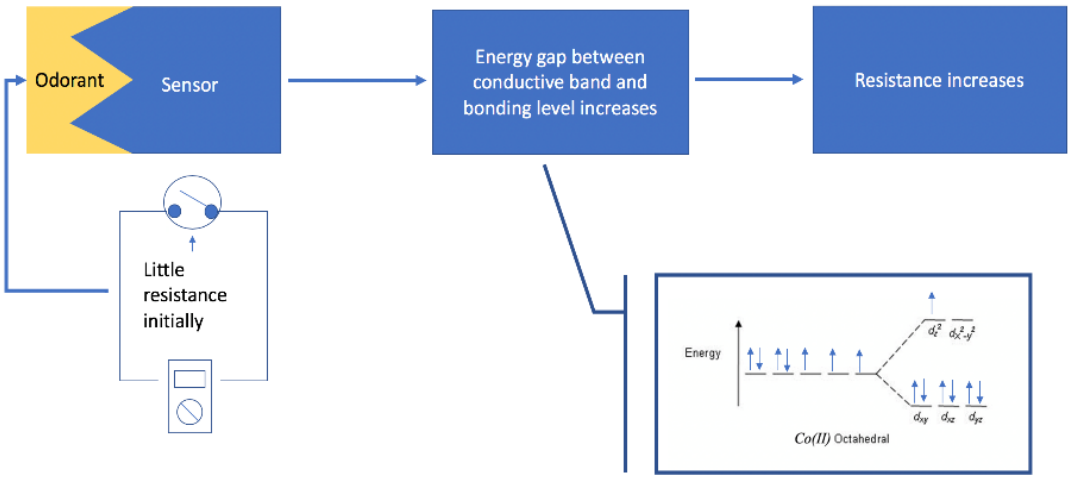


Figure 6. Flowchart of the experiment method

Results

Table 1. Change of resistance over time with no odorant

KΩ / Sec	Trial 1	Trial 2	AVERAGE of Control
0	4.96	8.52	6.74
30	3.33	6.54	4.94
60	1.94	4.98	3.46
90	1.67	3.86	2.77
120	1.00	2.99	2.00
150	0.52	1.94	1.23
180	0.33	1.28	0.81
210	0.21	0.91	0.56
240	0.14	0.35	0.25
270	0.10	0	0.05
300	0.06	0.00	0.03

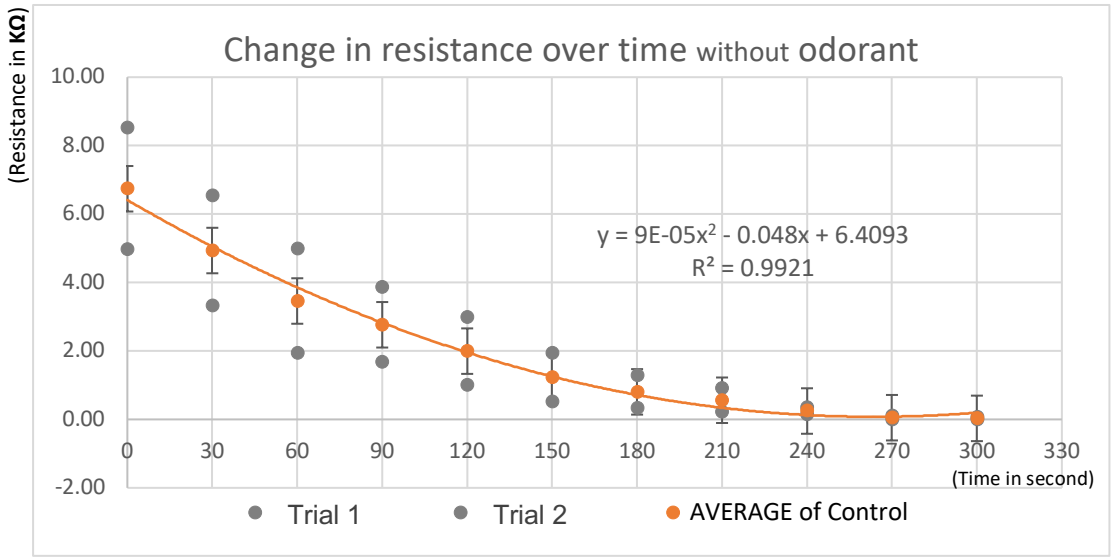


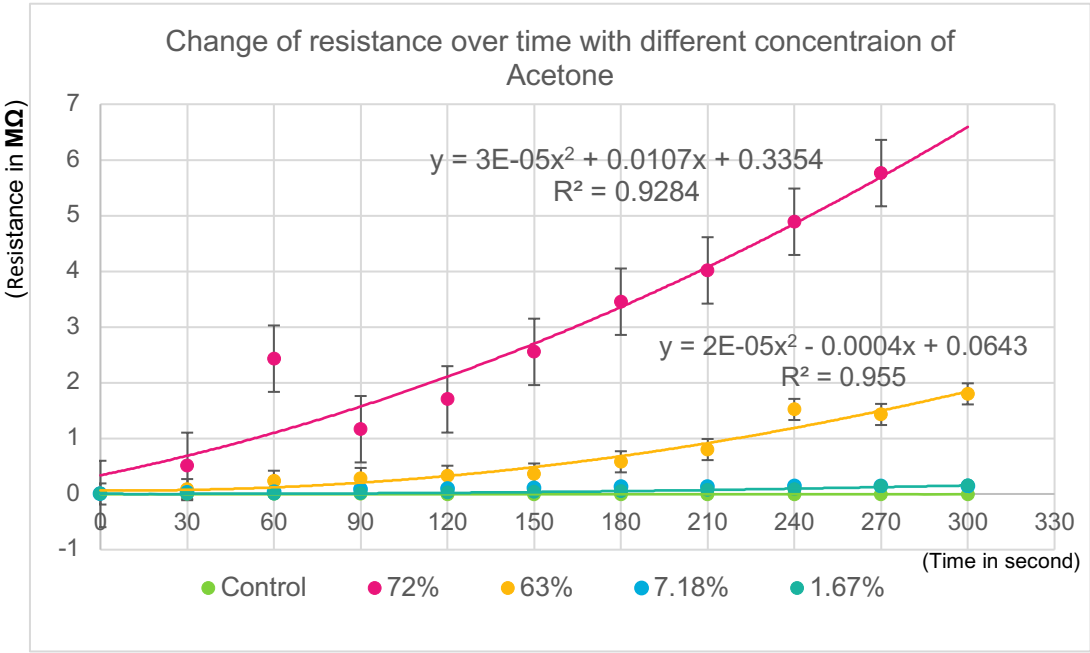
Figure 7. Change of resistance over time without odorant

Figure 7 is the control group of this experiment. This shows that the resistance has a quadratic decline without any odorant. The probable reason for this decline is the breakdown of acetic acid in the middle layer into positive and negative ions.

Table 2. Change of resistance over time with different concentration of Acetone (C_3H_6O)

MΩ / Sec	Control (0%)	72.0%	63.0%	7.81%	1.67%
0	0	0	0	0	0
30	-0.00198	0.505	0.078	0.02	-0.003
60	-0.00354	2.43	0.228	0.04	0.006
90	-0.00466	1.163	0.278	0.077	0.015
120	-0.00553	1.699	0.318	0.095	0.025
150	-0.00658	2.552	0.358	0.109	0.037
180	-0.00724	3.453	0.578	0.122	0.05
210	-0.00761	4.015	0.798	0.13	0.065
240	-0.00817	4.889	1.518	0.138	0.081
270	-0.00852	5.763	1.428	0.142	0.137
300	-0.00852	-	1.798	0.143	0.153

*Normalization was done due to the influence of the previous experiment.



*Normalization was done to show/compare the changes.

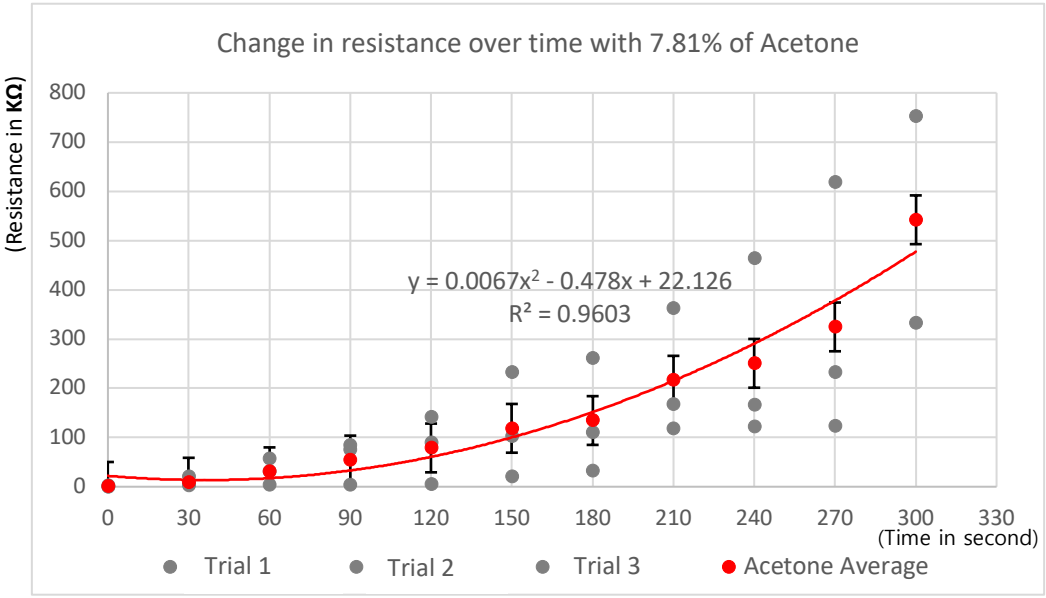
Figure 8. Change of resistance over time with different concentration of Acetone (C_3H_6O)

All graph in figure 8 showed similar trend, which was quadratic increase of resistance. The biggest increase was shown at 72% concentration of acetone, the highest tested, followed by 63%, then 7.81%.

Table 3. Change in resistance over time with 7.81% of Acetone

KΩ / Sec	Trial 1	Trial 2	Trial 3	AVERAGE
0	2.178	0	0	0.726
30	2.658	20	5	9.219
60	3.1126	57	31	30.371
90	3.776	75	84	54.259
120	5.2	89	142	78.733
150	20.85	102	233	118.617
180	32.38	110	261	134.460
210	167.9	118	363	216.300
240	165.8	122	464	250.600
270	232.8	123	618	324.600
300	332.4	-	752	542.200

*Normalization was done to show/compare the changes.



*Normalization was done to show/compare the changes.

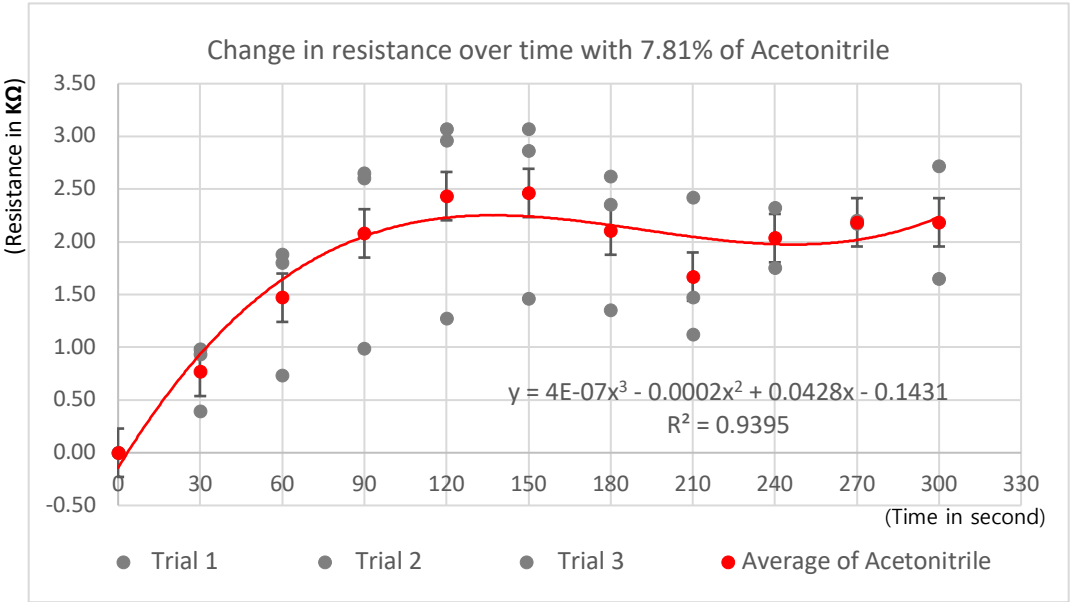
Figure 9. Change in resistance over time with 7.81% of Acetone

Figure 9 shows change in resistance of 7.81% of acetone. This showed a quadratic increase.

Table 4. Change in resistance over time with 7.81% of Acetonitrile (C_2H_3N)

KΩ / Sec	Trial 1	Trial 2	Trial 3	AVERAGE
0	0.00	0.00	0	0.000
30	0.39	0.93	0.98	0.767
60	0.73	1.80	1.88	1.470
90	0.99	2.60	2.65	2.080
120	1.27	3.07	2.96	2.433
150	1.46	3.07	2.86	2.463
180	1.35	2.35	2.62	2.107
210	1.47	1.12	2.42	1.670
240	1.75	-	2.32	2.035
270	2.17	-	2.2	2.185
300	2.72	-	1.65	2.185

*Normalization was done to show/compare the changes.



*Normalization was done to show/compare the changes.

Figure 10. Change in resistance over time with 7.81% of Acetonitrile (C_2H_3N)

Figure 10 indicates change in resistance over time with 7.81% acetonitrile instead of 7.81% of acetone as shown in figure 9. This graph represented a best fit of cubic increase; however, the trend indicates more of logarithmic increase. Detection started to plateau in approximately 2 minutes.

Discussion

Because the acetic acid in the middle layer can evaporate during the experiment, the initial resistance can be different for each trial. However, the change in resistance shows the same trends in the same group. Same sensor could be used up to three times, showing it was reusable. However, after three times, the detection was unstable.

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 figures 8, 9, and 10, an increase in resistance was seen, therefore, indicating that the odorant is attached to the detection site.

Hypothetically, the most ideal graph is a logarithmic function that increases rapidly in the beginning of the trials and starts to level out as time goes by. For example, as shown in Figure 10, the resistance went up rapidly for 2 minutes and started to level out. This indicates that odorant was fully detected by 2-3 minutes and did not show any more changes.

The graph 8 showed that the rate of change (the slope of the graph) increases as the concentration of the odorant increase. Thus, if the concentration of the odorant is high, the resistance also increases rapidly (Figure 8). This indicates that if there are higher concentration of odorant, more ligand binds to Cobalt, making the resistance increase rapidly. Concluding here, this electronic nose is able to compare and determine the concentration according to the rate of change.

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 therefore be more easily detected. Acetone having a higher polarity then acetonitrile can be the cause for such changes.

However, because Figure 9 didn't show the full ideal graph plateaus in 600 seconds, rather only showed increase, the reaction with acetone was slower than acetonitrile (Figure 10) which showed the full curve. Acetonitrile having long a bar-like atomic structure, whereas acetone has bends, can explain why the acetonitrile detected faster.

This research demonstrated a potential on detecting odorant using this method.

However, further investigation for variety of gases must be performed in order to develop a practical electronic nose that can detect various smell molecules in a mixture of gases.

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