

Self-Cleaning TiO₂ Sensor for Detection of Aliphatic and Aromatic Hydrocarbons

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Abstract:- Volatile organic compounds, as many air pollutants, can be potentially toxic for humans and animals. Titanium oxide-based sensors have been available over the past years as one method to detect such pollutants given the titanium oxide's photocatalytic properties and its ability to change its electrical conductance when binding various types of molecules. We constructed one type of such sensor and evaluated its ability to detect the presence of aliphatic and aromatic hydrocarbons in air as models of toxic organic compounds. Particularly, we used petroleum ether (PET) and naphthalene as our test model compounds. Being hydrophobic in nature, these compounds can significantly affect the electrical properties of a titanium oxide semiconductor layer, used as part of a sensor system, when they bind to it. The sensor's ability to "self-clean" after exposure to those compounds was also evaluated. UV light was used to induce such "self-cleaning" process as the absorption of UV photons by the sensor promotes the sensor's interaction with the organic molecules bound at its surface, ultimately leading to their destruction.

Key words: *Hydrophobic compounds, air contaminant, electrical conductance, semiconductor sensor, UV, photo catalysis*

1. INTRODUCTION

Air pollutants, like many volatile organic compounds, can be potentially toxic for humans and animals. A significant number of methods to detect these pollutants have been developed over the years. In particular, titanium oxide-based sensors have been available over the past years taking advantage of the titanium oxide's photocatalytic properties and its ability to change its electrical conductance when binding various types of molecules [1–3]. Its capacity to be used as a sensor for a good number of organic molecules in air has been well described in the literature [4-10]. Although its lack of specificity has been a drawback, it maintains a high potential as an inexpensive detection method with many qualities still to be explored and significant opportunities to seek sensing improvements and more adequate applications.

The focus of this study is centered on evaluating the ability of this type of sensor to self-cleaning in the presence of UV light and its availability of cyclic readiness to be reused

even with previous exposure to highly saturated vapors of an organic analyte. Our group did present some initial work in the past and we expand here. Two model hydrocarbon compounds were used in the study. First, in oil spills, like the massive "Deep Water Horizon" Gulf oil spill in 2010, tons of hydrocarbons are spewed into the air, creating a pressing need for rapid atmospheric petroleum screening assays. In particular, the volatile saturated aliphatic hydrocarbon chains (C1-C5 carbons long) in petroleum are difficult to detect. Our first model analyte, petroleum ether (PET), is a mixture of such compounds. Aliphatics do not absorb or emit light and are typically quantified using gas chromatography with electron capture detectors or with GC/tandem mass spectroscopy. Unfortunately, the preceding analysis involves significant time delays and costs. A titanium oxide sensor like the one used in this study can provide an inexpensive and sensitive alternative. On the other hand, heavier volatile hydrophobic aromatic organic compounds can be also very toxic when present in air. We use naphthalene vapor as our toxin model, and utilize air flow to facilitate its sublimation from its solid flake form. In general, our detection system is based on the variations of the measured electrical current through a TiO₂-coated interdigitated array electrode (CoIDAE) when exposed to each of the above analytes compared to a base line current when the CoIDAE is in regular ambient air. As indicated above, this detection system is intended to be a self-cleaning sensor in which the toxic compound that has attached to the coated electrode can be easily destroyed after detection has been made, leaving a clean sensor ready to be reused in new toxin detection.

2. MATERIALS AND METHODS

2.1 Titanium-Oxide Sensor

An interdigitated array electrode made of 64 interdigitated platinum fingers on a quartz substrate was used. In this array, each finger had a width of 10 µm and was separated from the adjacent fingers by 5 µm. From those 64 fingers, 32 were connected together to a terminal that could be considered the positive terminal, and the other 32 were connected together to a terminal considered the negative terminal. In the array structure, positive and negative

fingers alternated with 5 μm gap between them. The total array area was 3x2 mm. The array was sprayed with a titanium oxide coating prepared from a solution of 10 mg/ml of commercial P-25 powder (Evonik) containing 5 nm titanium oxide particles. The coating was created with five passes of our spraying device. With the P-25 coating,

the gaps between the platinum fingers were filled with titanium oxide that, once allowed to dry and calcined at 600° C for one hour, produced our final coated interdigitated array electrode (CoIDAE). Figure 1 below shows the array electrode.

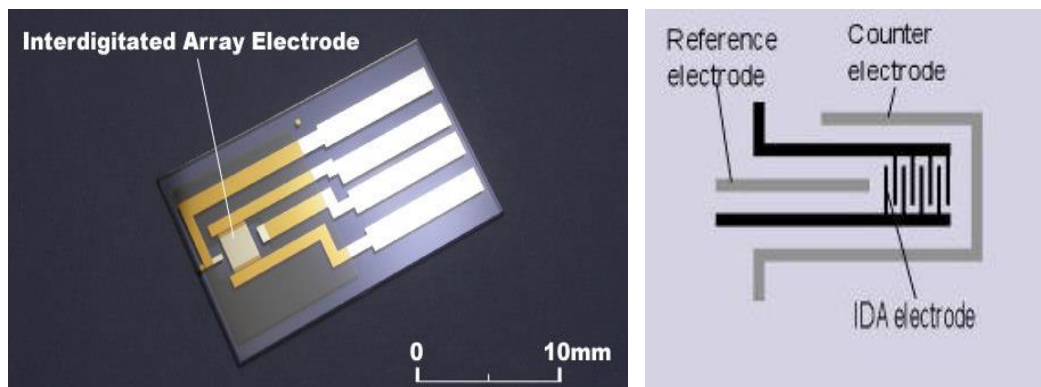


Figure 1. Picture (left) and diagram (right) of an Interdigitated Array Electrode (IDAE).

2.2 Experimental Setup and Procedure for Sensor Exposure to Vapors of the Liquid PET.

We used the TiO₂-coated interdigitated array electrode (CoIDAE) described above for detection of the PET compound. For this highly volatile liquid compound, we performed our detection tests in a large closed chamber consisting of an inverted glass bowl over a glass plate with a rubber seal between the bowl and the plate. There was no air flow during the detection tests. The CoIDAE and a pen UV lamp were located inside the chamber. The lamp was 1 cm away from the CoIDAE. (See Figure 2)

When testing the effect of PET vapors on our sensor, a liquid sample of PET on a small petri dish was placed and allowed to evaporate inside the sealed glass chamber. At this stage, the UV lamp was off to prevent photocatalytic destruction of any hydrocarbon compound that could attach to the CoIDAE. This was the exposure or test phase. Then

the chamber was opened and fresh ambient air allowed to fill back the chamber which was again sealed. The UV lamp was turned on to illuminate the CoIDAE with the intention of destroying and removing any hydrocarbons bound to its surface. This was the cleaning phase. The electrical current through the CoIDAE in response to a voltage pulse was measured every 12 minutes. As it was done in the case of naphthalene detection, for each measurement, a voltage pulse of 1 V was applied for 5 seconds to the CoIDAE and the resulting current was measured for 10 seconds by a digital multimeter and recorded in a computer using a LabVIEW program developed in our laboratory. Measurements were made in consecutive phases starting with an initial baseline of regular ambient air. Then consecutive cycles of PET evaporation in the chamber followed by fresh ambient air and UV illumination of the CoIDAE were carried out.



Figure 2. Experimental setup with the CoIDAE next to a petri dish containing the liquid PET that evaporates inside the glass chamber. The UV lamp for cleaning the sensor is also shown above the CoIDAE.

2.3 Experimental Setup and Procedure for Sensor Exposure to vapors from solid Naphthalene flakes

For the naphthalene detection, the setup was modified as sublimation of the solid flakes was accelerated with an induced air flow. The CoIDAE was placed inside an Erlenmeyer flask together with a pen UV lamp that illuminated the array from a fixed distance of 12 mm. At this distance, the UV lamp provided a light intensity of 2.5 mW/cm^2 . Two commercial small sensors for humidity and temperature were also placed inside the flask next to the CoIDAE to monitor relative humidity. The Erlenmeyer flask, which was sealed with a rubber stopper at the top, had a gas intake through a glass tube that passed through the rubber stopper and ended inside the flask at 2 cm from the bottom (see Figure 3). The Erlenmeyer also had a gas output on the side at the top, below the stopper, and was connected to a vacuum system that produced air flow inside the flask. The air flow could then be controlled by varying the vacuum applied. The intake at the top could take regular ambient air or could be connected to a

chamber filled with naphthalene flakes in a Teflon tube. In the latter case, air flow was forced to pass through the chamber with the naphthalene flakes and the naphthalene vapors had to go inside the flask and then out to the vacuum.

Air flow was always passing through the flask, controlled with the vacuum system. The electrical current through the CoIDAE in response to a voltage pulse was measured every 5 minutes. For each measurement, a voltage pulse of 1 V was applied for 5 seconds to the CoIDAE and the resulting current was measured for 10 seconds by a digital multimeter and recorded in a computer using the LabVIEW program developed in our laboratory. Measurements were made in consecutive phases starting with an initial baseline of regular ambient air. Naphthalene vapor was then passed and followed by a cleaning phase of regular ambient air again. The cycle of naphthalene application and cleaning was repeated several times.

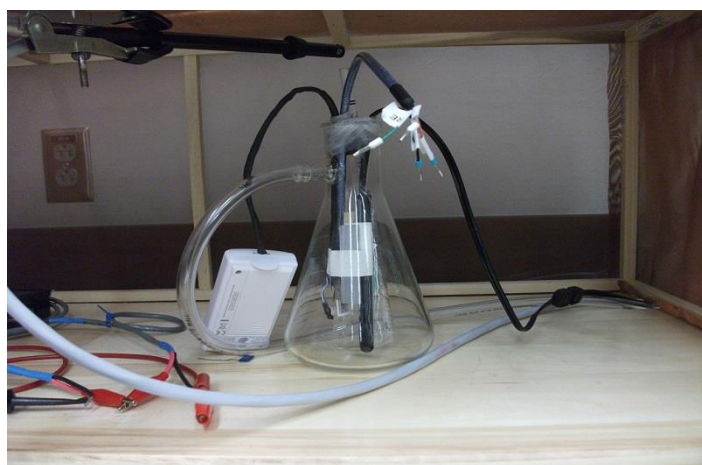


Figure 3. Experiment setup with a TiO_2 -CoIDAE contained within a sealed glass Erlenmeyer chamber. Also contained within this chamber is the UV light source (365nm Pen Ray, $\sim 3\text{-}5 \text{ mW/cm}^2$), a hygrometer sensor, and a temperature sensor. In photo to the right, one can see: temperature & hygrometer sensors (behind the CoIDAE), CoIDAE, UV lamp, and glass intake tube.

3. RESULTS

3.1 PET Detection

The results presented in Figures 4 and 5 below show that the exposure to the PET decreases the sensor current to half or less than half of the original base value, which was obtained from controls with no PET. That original value was recovered with the application of UV light. The results for two cycles of PET evaporation in the chamber and subsequent cleaning with regular ambient air are shown in Figure 4. In the graph, the peak current is presented for each measurement made every 12 minutes over a period of 5 hours. The initial blue curve corresponds to the initial base line with regular ambient air, the red curves correspond to the phases during which PET was allowed to evaporate in the chamber and the UV lamp was kept off,

and the green curves correspond to the cleaning phases with fresh ambient air back in the chamber and the UV lamp on illuminating the coating. For our initial base line conditions, the measured peak currents were around 500 nA. When PET was allowed to evaporate inside the chamber, the measured peak currents dropped to 200 nA or below in a period of 25 minutes. During the cleaning phases the peak currents returned to 500 nA. Since there was no air flow in these experiments, peak current values took time to stabilize in the new environment as the internal relative humidity took time to stabilize itself.

The results presented in Figure 5, for a separate set of runs, corroborate what is seen in Figure 4: the reduction of electrical conductivity during exposure of the sensor to PET vapors and the recovery of the conductivity values after UV illumination and no more presence of PET.

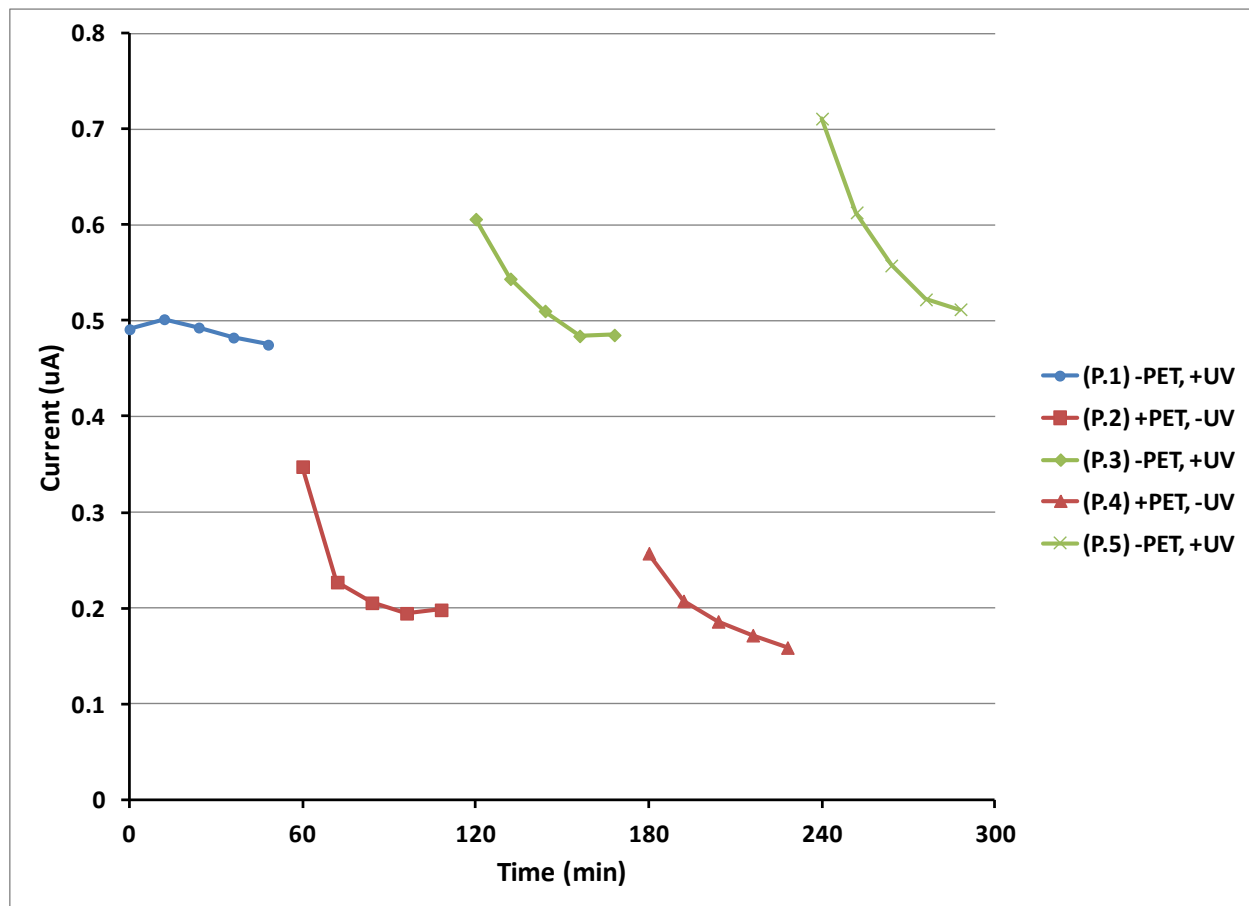


Figure 4. This graph shows the effect of aliphatic hydrocarbon vapors, originally present in a sample of petroleum ether (PET), on our sensor system. The points represent peak electrical currents through a TiO_2 -coated interdigitated array electrode (CoIDAE) in response to 5s-1V voltage pulses applied with 12-minute time intervals. The CIAE and a lamp for UV illumination were inside a closed glass chamber with the presence or absence of a PET. The initial blue curve corresponds to a regular ambient air environment. The red curves correspond to the presence of PET vapors inside the chamber. The green curves correspond to cleaning of the sensor by restoring the regular ambient air environment and turning on the lamp for UV illumination of the CoIDAE.

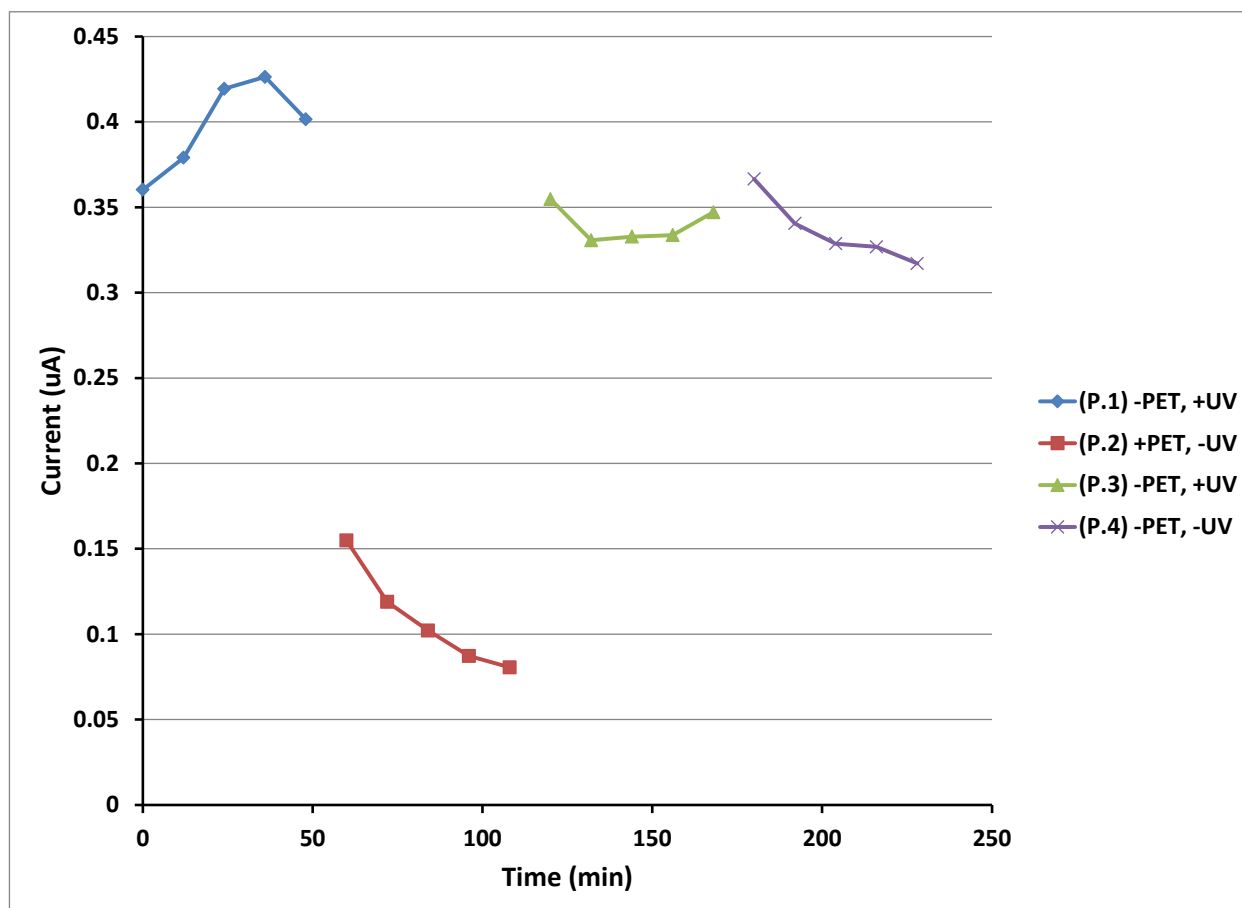


Figure 5. Our TiO_2 -CoIDAE sensor interface signals the presence of petroleum ether and shows self-cleaning behavior during UV illumination. Each data point represents the peak current yielded from the 5s-1V pulse applied during its corresponding run. The second phase (P.2) shows a significant decrease in electrical conductivity during exposure to PET vapor. The conductivity returns to original P.1 levels with UV illumination in phase three (P.3). The last phase (P.4) represents a control run, which shows that there is no effect when performing a series of runs with no UV illumination and no exposure to PET

3.2 Naphthalene Detection

The results for two cycles of naphthalene pass and subsequent cleaning with regular ambient air are shown in Figure 6 below. In the graph, the peak current is presented for each measurement made every 5 minutes over a period of 3 hours and 15 minutes. The initial blue curve corresponds to the initial base line with regular ambient air flowing through the flask, the red curves correspond to the passing of naphthalene vapors, and the green curves correspond to the cleaning phases passing again regular ambient air. For the cleaning phases, air flow had to be increased in order to achieve faster removal of naphthalene. The first pass of naphthalene vapor reduced the peak current from 360 nA to only 10 nA and remained around that value during the naphthalene application and the initial part of the cleaning phase with ambient air. It was required to increase the air flow during the cleaning phase to speed up the process of naphthalene removal. The increased flow produced an increase in the relative humidity to 36% from the original base line of 33%. Even though the humidity

returns to base line values 15 minutes after initiating the cleaning phase, the electrical conductivity through the CoIDAE does not recover at all in that period most likely due to remaining naphthalene bound to the titanium oxide coating. Depending on the amount of air flow that was used for the cleaning, between half an hour and one hour was required to increase the current back to and above the original base line values. At the end of the cleaning phase, the peak currents were higher than the initial base values due to the combination of increased humidity produced by the higher air flow used to speed up the cleaning, the application of UV light, and the removal of naphthalene from the sensor. Values of 650 nA were measured at the end of the first cleaning phase. A second pass of naphthalene vapors produced, once again, a dramatic drop of the currents down to around 10 nA with the subsequent recovery to peak currents above 700 nA at the end of the second cleaning phase. We found that the results described above were reproducible every time with no observable damage or degradation of the electrode.

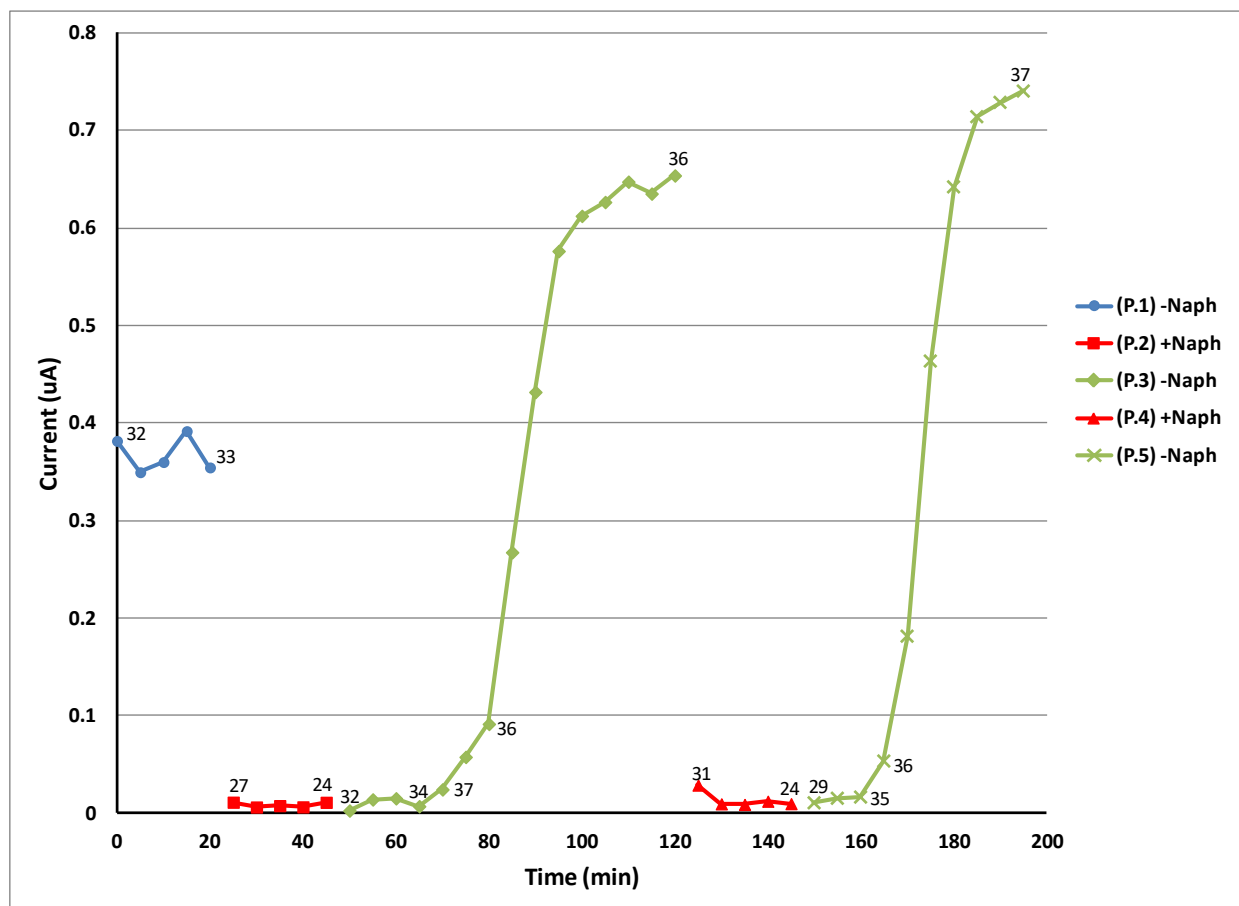


Figure 6. This graph shows the effect of naphthalene vapors on our developed sensor system. The points represent peak electrical currents through a TiO_2 -coated interdigitated array electrode (CoIDAE) in response to 5s-1V voltage pulses applied with 5-minute time intervals. The CoIDAE and the lamp for UV illumination were inside an Erlenmeyer flask with continuous air flow. The numbers next to the curve points are values of relative humidity. The initial blue curve corresponds to regular ambient air with starting humidity of 32-33%. The red curves correspond to the passing of naphthalene vapors. The green curves correspond to cleaning of the sensor with increased flow of ambient air.

4. DISCUSSION

In this study we confirmed that the use of titanium oxide as a sensor constitutes a simple and relatively inexpensive method to detect hydrophobic molecules, potentially toxic, in ambient air. This is consistent with results presented by other investigators that have used titanium oxide for detection of a variety of compounds. This study shows, however, in a more particular way, the self-cleaning capabilities and the cycling reproducibility of this sensor consisting of the thin titanium oxide layer covering an interdigitated array electrode. This combination of components provides robustness, durability, and reliability to the detection method. With the combination of UV light and continuous flow of regular air we have produced a self-cleaning sensor that can be reused many times without significant observable degradation. UV light illumination of the coating is an essential part of the process of cleaning the sensor due to the photocatalytic properties of the titanium oxide that lead to destruction of an organic compound bound to the coating. Beyond that fact, we observed that, maintaining more constant UV illumination of the coated array actually enhanced the detection

sensitivity by producing the observed dramatic drop in conductivity when the coating interacted with the hydrocarbon present in the air. This effect was more obvious in the case of naphthalene. As one possibility, the UV light could enhance the binding of naphthalene to the titanium oxide coating and facilitate consumption by the naphthalene of UV-generated electrons in the process of its own photocatalytic destruction, removing those electrons from circulation and greatly reducing the electrical conductivity of the coating. Furthermore, we confirmed the capability of this sensing system to detect both aliphatic and aromatic types of hydrocarbons. Another important point to be mentioned is the aspect of specificity. Although the sensor has not shown clear specificity for a particular compound, more tests of electrical conductivity need to be performed with other organic molecules in order to search for well-defined differences in electrical response. Additionally, it may be possible to achieve specificity by varying and refining the coating properties on the array electrode as well as by modifying the characteristics of the cleaning process that may be dependent on the type of analyte bound to the coating. This sensor has great potential to be used in the field as air samples can be easily

taken and tested. Any hydrophobic compound detected in the air is potentially toxic since hydrophobic compounds should not be present in a normal air environment. This sensor could be used in an area affected by an oil spill or other circumstances that produce air contamination with hydrocarbon vapors which become a health hazard or a potential risk for hydrocarbon explosions due to leaks from pipes and other reservoirs. More work needs to be done to seek more specificity on the type of compound that the sensor detects.

5. CONCLUSION

The titanium oxide sensor used in this study can adequately detect both aliphatic and aromatic hydrocarbons, can clean itself in the presence of UV light, and can be reused many times with high reproducibility.

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6. REFERENCES

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