รายงานวิจัยฉบับสมบูรณ์

(15 กันยายน 2551 – 14 กันยายน 2554)

โครงการ เซ็นเซอร์ตรวจวัดก๊าซเคมีแบบลูกครึ่ง

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เดือน ปี ที่เสร็จโครงการ *กันยายน 2554*

สัญญาเลขที่ BRG5180023

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สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย

(ความเห็นในรายงานนี้เป็นของผู้วิจัย สกว.ไม่จำเป็นต้องเห็นด้วยเสมอไป)

กิตติกรรมประกาศ

ผู้วิจัยขอขอบพระคุณผู้มีส่วนทำให้โครงการวิจัยนี้ประสบความสำเร็จสมความมุ่งหมาย ความสำเร็จของโครงการนี้นอกจากจะเป็นไปตามเจตนารมณ์ของ สกว. แล้ว ยังมีผลต่ออนาคตในวิชาชีพของผู้วิจัยเป็นอย่างยิ่ง ผู้วิจัยใคร่ขอขอบพระคุณท่านเหล่านั้นดังรายนามต่อไปนี้

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และสุดท้ายนี้ผู้วิจัยขอขอบคุณครอบครัวได้แก่ คุณจุฑา เกิดเจริญ ภรรยา ด.ญ. อะตอม เกิดเจริญ ธิดา และ ด.ช. พฤกษรักษ์ เกิดเจริญ บุตร ที่เข้าใจและเสียสละให้ผู้วิจัยได้ใช้เวลาทุ่มเทกับการทำงานวิจัยได้อย่างเต็มที่

ธีรเกียรติ์ เกิดเจริญ

15 กันยายน 2554

ABSTRACT

Project Code : BRG5180023

Project Title : Hybrid Chemical Gas Sensors

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Project Period : September 15th, 2008 – September 14th, 2011

Thailand has profited from her rich biodiversity and diverse geography that makes this country to own a lot of uniquely geo-specific agricultural products. Aroma characteristics, as a result of bio- and geo-specificities, have been used to identify and classify the quality of foods and beverages, thus determining the value and price. Various food industries use smell as an indicator for the quality of fresh foods, i.e., meat and sea-food products, by employing human's sensory evaluation and gas chromatography techniques, although such techniques are quite expensive and prohibitive for most local industries. Such problems call for a new approach to evaluate flavor and smell based on machine olfaction. Machine olfaction is a concept of automated evaluation / identification / discrimination of aroma or smell using an array of chemical gas sensors. The so-called "electronic nose" device built from such sensors is similar to the working principles of a dog's nose. It can detect small amount of odor molecules. Electronic nose employs an array of chemical gas sensors, numbering from 2 up to hundred sensors. In this research, we will develop novel chemical gas sensors that are sensitive and specific to volatile organic compounds found in Thai agro-food products. Although global research on this subject is highly competing, our team will propose a freshly new idea on development of "hybrid" chemical gas sensors that employs the goodness of inorganic and organic sensing materials together with hybridized transduction methods. First, basic understanding on the working principles of chemical gas sensors based on hybrid inorganic and organic sensing materials will be obtained by doing fundamental research, in order to design unique and novel chemical gas sensors. Then, the knowledge will be used to fabricate and develop efficient chemical gas sensors that have high selectivity and sensitivity to basic volatile organic compounds. Finally, an electronic nose device based on an array of newly developed chemical gas sensors will be constructed and tested with Thai foods and agricultural products.

Keyword: Chemical sensor, organic electronics, electronic nose, porphyrin, carbon nanotube

บทคัดย่อ

รหัสโครงการ: BRG5180023
ชื่อโครงการ: เซ็นเซอร์ตรวจวัดก๊าซเคมีแบบลูกครึ่ง
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ประเทศไทยมีความหลากหลายทางชีวภาพรวมทั้งมีความร่ำรวยในความแตกต่างทางภูมิศาสตร์ จึงทำให้ประเทศไทยมีผลิตภัณฑ์ทางการเกษตรและจากธรรมชาติที่มีความเป็นเอกลักษณ์ เฉพาะถิ่น มีรสชาติและกลิ่นที่แตกต่างไป ซึ่งกลิ่นและรสชาติเหล่านี้นี่เองเป็นตัวกำหนดมูลค่าของผลิตภัณฑ์เหล่านั้น อุตสาหกรรมอาหารทั้งหลาย มักจะใช้นักดมและนักชิมเป็นผู้ควบคุมคุณภาพของผลิตภัณฑ์ ซึ่งนอกจากจะมีค่าใช้จ่ายที่ค่อนข้างสูงแล้ว ยังขาดความแน่นอนคงที่ในแง่ของการตรวจวัด ซึ่งกำหนดมาตรฐานไม่ได้ ทำให้อุตสาหกรรมอาหารทั้งหลายมีความต้องการเทคนิคหรือเครื่องมือที่สามารถตรวจวัดกลิ่นอาหารแทนมนุษย์ได้ โครงการวิจัยนี้ได้สร้างเครื่องมือดังกล่าวที่มีชื่อว่า “จมูกอิเล็กทรอนิกส์” ซึ่งมีหลักการทำงานคล้ายจมูกของสัตว์เลี้ยงลูกด้วยนม โดยประกอบด้วยเซ็นเซอร์ตรวจวัดกลิ่นตั้งแต่จำนวน 2 เซ็นเซอร์เป็นต้นไป โครงการวิจัยนี้ ได้ทำการพัฒนาเซ็นเซอร์ตรวจวัดกลิ่นชนิดใหม่ ที่มีความเหมาะสมต่อผลิตภัณฑ์ในประเทศไทย ซึ่งเซ็นเซอร์หัววัดที่พัฒนานี้จะเป็นเซ็นเซอร์แบบลูกครึ่ง ที่สร้างจากวัสดุผสมระหว่างสารอินทรีย์กับสารอนินทรีย์ รวมถึงเทคนิคการตรวจวัดผสมผสานระหว่างเทคนิคทางไฟฟ้าและเทคนิคทางแสง เพื่อที่จะนำไปสู่เป้าหมายดังกล่าว โครงการนี้ได้มีการวิจัยอย่างครบวงจร ตั้งแต่งานวิจัยพื้นฐานเพื่อนำไปสู่ความเข้าใจในการทำงานระดับโมเลกุลของเซ็นเซอร์ การออกแบบวัสดุที่ทำงานเป็นเซ็นเซอร์ตรวจวัดกลิ่น อันตรกริยาระหว่างกลิ่นกับเซ็นเซอร์ องค์ความรู้พื้นฐานเหล่านี้ได้ถูกนำมาใช้ในการสร้างและประกอบอุปกรณ์เซ็นเซอร์และเครื่องจมูกอิเล็กทรอนิกส์ ที่มีความไวและความจำเพาะกับกลิ่นที่สนใจ โดยมีเป้าหมายไปที่ผลิตภัณฑ์ทางการเกษตรของไทย

คำสำคัญ: เซ็นเซอร์เคมี อินทรีย์อิเล็กทรอนิกส์ จมูกอิเล็กทรอนิกส์ พอร์ไพริน ท่อนาโนคาร์บอน

EXECUTIVE SUMMARY

Thailand has a big advantage on her rich biodiversity and diverse geography. The country owns a lot of geo-specific agricultural products such as foods, beverages, medical herbs and products. In fact, it is the aroma molecules contained in those products that makes them unique and bio- and geo-specific. Aroma characteristics have been used to identify and classify the quality of foods and beverages such as wines, beers, tea, coffee, etc, thus determining the value and price. Various food industries use smell as an indicator for the quality of fresh foods, i.e., meat and sea-food products. To serve those aims, the industries have usually employed human's sensory evaluation and gas chromatography techniques, although such techniques are quite expensive and prohibitive for most local industries. We had once visited a shrimp-freezing factory in Samutsakorn Province and observed a human-based evaluation of the freshness of in-coming shrimps delivered from a shrimp farm. Acceptance or rejection of the whole container was totally based on justification of a single human judge by smelling the random shrimp samples. Based on the interview with the judge, justification of the freshness of shrimp samples is admittedly rather risky and suspicious both for the industry and the farmer. The nose of well-trained human judge is very sensitive but not reliable because it can be easily disturbed by external factors such as emotion, time of day, workload etc. We had also an opportunity to visit a Thai winery near Khao Yai national park. The winemaker there employed his sensory evaluation by tasting and smelling the fermented products from time to time to evaluate the best bottling and consuming time. This process is day-to-day and quite laborious which is inevitably prone to human error.

The above-mentioned problems call for a new approach to evaluate flavor and smell based on machine olfaction. Machine olfaction is a concept of automated evaluation / identification / discrimination of aroma or smell using an array of chemical gas sensors. The so-called "electronic nose" device built from such sensors is similar to the working principles of a dog's nose. It can detect small amount of odor molecules. It will be able to learn, memorize and recognize pattern of good/bad quality of products. Basically, appropriate mixing of molecules that make taste and smell in foods and beverages is the key for human's deliciousness. Electronic nose could be used to study and maintain that quality, thus replacing specially well-trained personals. Surprisingly, there are quite a few research teams in Thailand working on this subject, despite there are so rich applications in our country.

Electronic nose employs an array of chemical gas sensors, numbering from 2 up to hundred sensors. Research on chemical gas sensors is focused on two issues: selectivity (specificity to a molecule or a class of molecules) and sensitivity (strength of signal upon exposure to low concentration of molecules). Until recently, most chemical gas sensors used in Thailand have been imported from abroad. Such sensors are not suitable for Thai agro-food products because they are mostly designed for other industries such as petrochemicals, automobile and environment. In other words, the selectivity and sensitivity of most imported chemical gas sensors have been tuned for detecting gases (almost inorganic gases) observed in those (heavy) industries. The flavor and smell molecules contained in food and agricultural products are usually volatile organic compounds (VOCs) which are very rich in diversity. Development of novel chemical gas sensors that are selective and sensitive to these compounds requires fundamental research involving several basic science subjects: to name a few, thermodynamics of gas-solid surface interactions, electronic structure of sensing materials and transducing mechanisms etc. Although global research on this subject is highly competing, our team assumes the advantage on geography in that we are closer to the availability of problems and products. Furthermore, we have proposed a new idea on development of "hybrid" chemical gas sensors that employs the goodness of inorganic and organic sensing materials at the same time (In general, most research groups work either on inorganic or organic materials, but we have experience for both). Basic understanding, especially in the physics of how sensor works, is also our uniqueness, which is believed to create high impact academic publications and innovation.

This project has been completed with 6 international publications (indexed in ISI database), 11 international proceeding papers (indexed in SCOPUS), 2 prototypes (amine sensors and hand-held electronic nose device) and 1 Thai patent. The prototypes and patent can further be developed for commercialization in the future.

เนื้อหางานวิจัย

1. OBJECTIVE

(1) Develop basic understanding on the working principles of chemical gas sensors based on hybrid inorganic and organic sensing materials and design novel chemical gas sensors

(2) Fabricate and develop efficient chemical gas sensors using the understanding obtained from (1), which have high selectivity and sensitivity to basic volatile organic compounds

(3) Develop an electronic nose device based on an array of chemical gas sensors obtained from (2) for analysis of foods and agricultural products.

2. LITERATURE REVIEW

Thailand has a big advantage on her rich biodiversity and diverse geography. The country owns a lot of geo-specific agricultural products such as foods, beverages, medical herbs and products. In recent years, the country has become one of the world's leading food and beverage exporters. In general, the big industries usually employ various analytical methods such as human sensory evaluation[1], gas chromatography[2], nuclear magnetic resonance[3] and mass spectrometry[4], to assess quality control standards of foods and beverages. These methods are reliable, but they are quite time-consuming, complicated and so costly that SMEs (small and medium enterprises) or local industries are reluctant to adopt the technologies, especially if they just want to perform quick screening of the products.

Recent decades have observed significantly increasing interest in the applications of electronic nose (E-nose) for qualitative analysis of odors. The first E-nose experiments were

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conducted in the early 1990s[5,6]. Since then, E-nose has become a powerful tool to complement or even replace traditional chemical analysis in many applications ranging from quality control of foods[7,8] and beverages[9,10], environment protection[11] to public safety[12]. Electronic nose employs an array of chemical gas sensors, numbering from 2 up to hundred sensors. Research on chemical gas sensors is focused on two issues: selectivity (specificity to a molecule or a class of molecules) and sensitivity (strength of signal upon exposure to low concentration of molecules). Chemical sensors can be classified into 4 types[13] based on their transduction, a mechanism that converts chemical interaction into a sensor signal: (1) Optical, (2) Thermal, (3) Electrochemical and (4) Gravimetric. Most of research works on chemical gas sensors done by other groups in Thailand have so far been mainly based on the electrochemical transduction because its interface setup is not complicated and can be done by simple facility.[14,15,16,17] In contrast, our research team has experience on optical-[18,19], electrical-[20,21] and gravimetric-based[22] chemical sensors.

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Electrical transduction is the most popular among the transduction techniques because of its simplicity. As a result, most commercial chemical gas sensors adopt this technology and metal oxide semiconductors assume the most used sensor architecture due to their low-cost, high sensitivity and simplicity in function.[23] Thus, one could easily combine several functional elements such as sensitive layer, signal converter and control electronics in the same device. Notwithstanding the simple working principles of metal oxide gas sensors, the gas-sensing mechanism at the microscopic level is quite complex and so far insufficiently understood.[24,25] The gas sensors having the same metal oxide materials can have completely different gas-sensing properties depending on the preparation conditions. It is firmly believed that the chemo-resistive change of the metal oxides is caused by catalytic redox reactions at the sensing surface. Such reactions are controlled by electronic structure, chemical composition, crystal structure and relative orientation of the oxide surface to the analyte molecules, thereby allowing tuning their gas-sensing properties by modifying such parameters.[26] Structural engineering by reducing grain size and modifying crystallite microstructure has been widely accepted as the best method to optimize the metal oxide gas sensors.[27]

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Among the metal oxides, zinc oxide and tin oxide have been the most frequently used materials in solid-state gas sensors. Sensitivity and selectivity of these materials can be tuned on the basis of structural engineering. Tin oxide owns a rich set of structural parameters which makes it so complex to be controlled. For examples, tin oxide nanocrystals obtained from a spray pyrolysis experiment can have so many crystallographic planes such as (110), (111), (200), (101), (011), (-1,-1,2) etc.[28] Such crystallographic parameters are sensitive to the change in grain size responsible for different gas-sensing properties of the films prepared using different conditions.[29] Metal oxides can be doped by a small amount of metals, such as Sn, Pd, Cu, Nb etc, in order to modify the structural and electronic properties. It was found that doping tin oxide with Sn, In and Nb leads to decreasing the grain size down to the nanometer regime.[30] Kawamura et al has found that the inter-play between different crystal growth directions can be controlled by addition of impurities.[31] Besides pure metals, metal oxides can be doped or mixed with organic materials, leading to the so-called "hybrid" chemical gas sensors. The field of hybrid chemical gas sensor is still at the infant stage.[32] Combining both the hard and soft materials into a single film is quite challenging due to complication both in the preparation and fabrication processes.[33] In this research, we are specifically interested in the hybridized metal oxide gas sensors based on carbon nanotubes and metallo-porphyrins [34,35] because we have experienced in both materials and there have been still early development on this issues.

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For optical-based chemical gas sensors, we have previously worked on the optically active organic sensing materials – porphyrins and phthalocyanines.[18] The optical based technique that measures optical change in selected wavelength regions arranged in an array configuration is very efficient sensor architecture.[36] Hence, the measurement setup can be easily adapted from the commercial UV-Visible spectrometer by replacing the standard sample stage with a dynamic-flow gas chamber. The large family of phthalocyanines and porphyrins allows a wide range of applications for gas sensing such as alcohol[36], nitrogen monoxide[37], nitrogen dioxide[38], acetone, acid[39], amine (which is produced by decomposition of fish and seafood)[40], tobacco smoke[41] and the four types of Spanish olive oils[42]. In our previous work, zinc phthalocyanine was investigated as sensitive materials for alcohol detection.[18] A mechanism underlying the gas sensing was theoretically studied and proposed to involve ion-dipole interactions between gas molecule and phthalocyanine base. Another work of ours reports that zinc phthaocyanine and zinc porphyrin are sensitive to various functional organic compounds such as ketone, aldehyde and acid, allowing them to be sensing materials for foods and beverages.[43]

In this research project, we have developed new hybrid chemical gas sensors based on three components: metal oxides (tin oxide), organic additives (carbon nanotubes and

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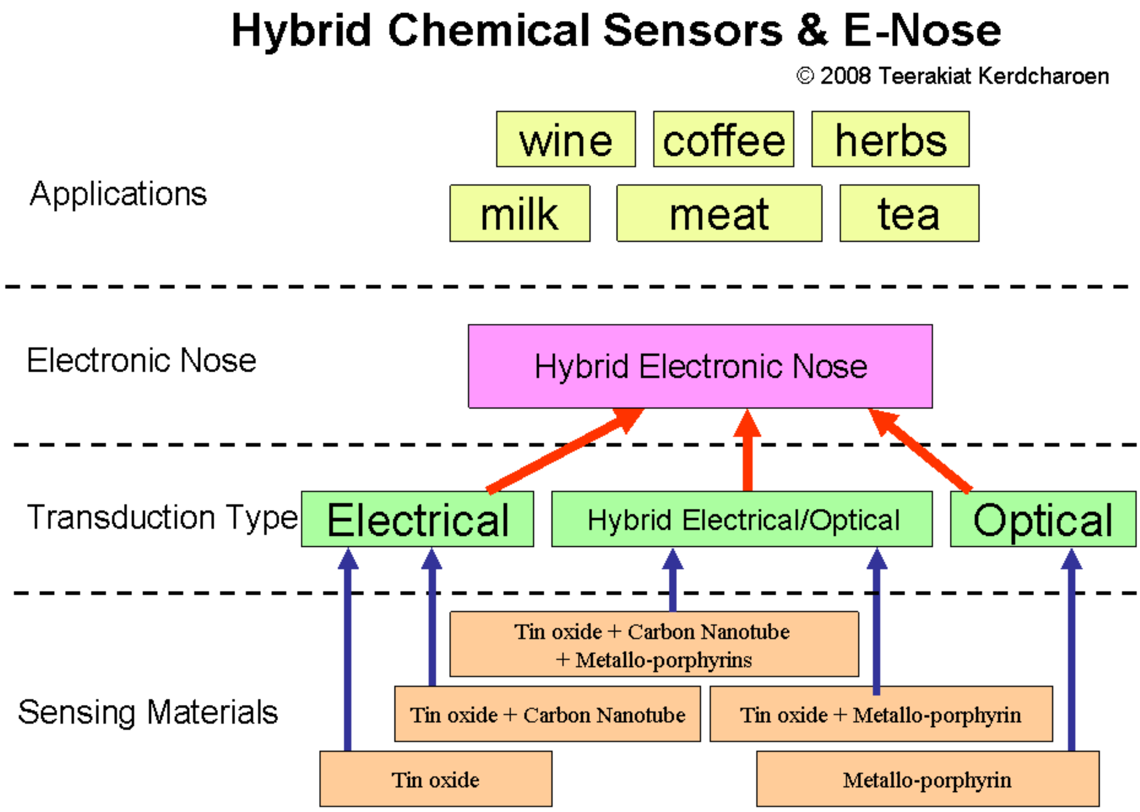
metallo-porphyrins) and metal additives (K doped in carbon nanotube). We will demonstrate the newly developed chemical gas sensors in the field of food and agriculture. Electronic nose device will be used as a platform for testing the sensors.

3. METHODOLOGY



The Overview of this Project

Phase I: Research on new native and hybridized inorganic-organic sensing materials

At this stage, various sensing materials will be investigated. We will explore how to prepare these sensing materials properly. Microstructure, electrical properties, optical properties and gas-sensing properties will be studied using various techniques: SEM, TEM, IR, AFM, UV-Vis, Resistivity, XRD, XPS, XANES etc.

- **Native tin oxide:** This material can be prepared by sputtering technique. This sensing material is used for benchmarking of new chemical sensors to be discovered.
- **Metallo-porphyrins:** The sensing layer can be prepared by spin coat. We will investigate the possibility of tuning gas-sensing properties of these materials by varying composition of different species of metallo-porphyrins.
- **Tin oxide / CNT composites:** The sensing layer can be prepared by electron beam evaporation and/or coating CNT matrix onto the tin oxide top layer. We will investigate the variation in sensitivity and selectivity of the hybridized sensing materials upon change in the functional group of functionalized CNTs. Fundamental research will be carried out to obtain understanding of the gas-sensing mechanism.
- **Tin oxide / metallo-porphyrins:** The sensing layer can be prepared by coating of the tin oxide top layer with metallo-porphyrins matrix. We will investigate the sensitivity and selectivity of the resulting sensing materials upon change in the metal center and/or peripheral groups on porphyrin rings. Fundamental research will be carried out to obtain understanding of the gas-sensing mechanism.
- **Tin oxide / CNT / metallo-porphyrins:** These composite materials are the most complex in this project. It will be the outcome of well-defined understanding of all above-mentioned native and composite materials. These materials are novel in which they have never been reported.

Phase II: Development of native and hybrid chemical gas sensors

At this stage, chemical gas sensors will be fabricated using the newly developed sensing materials. Electrical transduction will be employed for 2 types of sensing materials: native SnO_2 and SnO_2/CNT composite. Optical transduction will be used for metallo-porphyrin sensing materials because only this type of sensing materials in this research is optically active. Hybrid electrical-optical transduction will be employed for SnO_2/metallo-porphyrin and SnO_2/CNT/metallo-porphyrins composites. Gas-sensing properties of 5 types of chemical sensors will be tested. Selectivity and sensitivity of these sensors to which gas molecules they response most will be searched and mapped. The results at this stage will be fed back to the fundamental research of Phase I for further improvement of the chemical sensors.

Phase III: Development of hybrid electronic nose

At this stage, an electronic nose device will be constructed from newly developed chemical gas sensors. The E-nose will be installed at a winery for routine examination of fermented wines. Electronic set-up and software will be developed for at-line monitoring. Other applications besides wines, namely milk, meat, herbs, tea and coffee, will be explored.

Scientific techniques involved in this project

- AFM (atomic force microscopy): This technique will be used for analysis of the thin film morphology (roughness, grain size, chemical composition distribution). The film thickness can also be measured using this technique. Results from this technique will help to understand the dependence of preparation parameters to the film properties.
- SEM (scanning electron microscopy) and TEM (tunneling electron microscopy) will be employed to investigate the structural properties of the film (roughness, grain size distribution, porosity), especially for the composite materials (e.g., SnO_2/CNT).
- XPS (X-rays photoemission spectroscopy) and XANES (X-rays absorption near-edge structure) will be utilized to investigate the electronic structure of the metallo-porphyrin thin films, the interactions of the thin films with volatile organic compounds, the microstructure of the films (molecular orientation).
- DFT (Density functional theory) calculations will be used to study the interactions between the sensing materials (SnO_2, CNT, metallo-porphyrin)

with volatile organic compounds. The method will give both quantitative and qualitative pictures of the interactions which helps reducing the design process of the chemical sensors.

- Molecular dynamics (MD) simulations will be employed to study the surface properties of the metallo-porphyrin films, e.g., molecular orientation, molecular distribution etc. It will be the first time that the method being employed to gain insight into the working mechanism of this type of sensors.
- UV-Vis (ultraviolet visible) spectroscopy will be used to probe the electrons near the frontier electronic states. These electronic states are very sensitive to external disturbance by molecular interactions. Therefore, we use this technique to probe the interactions between metallo-porphyrins with volatile organic compounds. Change in the optical absorption is exploited as optical gas sensor.
- IR (infrared) and Raman spectroscopy based on absorption and/or reflection will be employed to detect organic functional groups on thin films. This technique will be used to probe the degree of functionalization of hybridized organic-inorganic sensing materials. Infrared spectra are outcomes of molecular vibration which yields different patterns for various functional organic compounds: alcohol, ketone, acid etc.
- XRD (X-rays diffraction) spectroscopy will be employed to investigate the crystallographic phase in the thin films, especially for metallo-porphyrin thin films since these thin films must be pre-treated either by thermal annealing or solvent vapor exposure prior to employment as gas-sensing materials. XRD will give information about molecular orientation in the films that reflects stability of the films.

Scope of research starting from materials, methodology to applications is defined in the following table.

Class of chemical sensors	Hybrid inorganic-organic
Inorganic sensing materials	Metal oxide semiconductor: SnO_2
Organic sensing materials	Carbon nanotubes (multi-walled) and metallo-porphyrins
Fabrication of sensing materials	E-beam evaporation, sputtering, spin coat, drop cast
Transduction types of sensors	Primarily electrical (chemo-resistive) which may be additionally combined with optical (measuring reflectivity change)
Targeted analytes	Volatile organic compounds (VOCs): alcohol, ketone, organic acid, ester, ether
Targeted applications	Wines, milks, coffee, tea, meat
Odor recognition methods in electronic nose	Principal component analysis (PCA) and artificial neural network (ANN)

4. RESULTS AND DISCUSSION

Au-doped Zinc Oxide Nanostructure Sensors

Pure and 10% w/w Au-doped Zinc oxide (ZnO) nanostructure sensors were produced and used as sensing devices in a portable electronic nose (E-nose). The nano-sensors were prepared using thermal oxidation technique with sintering temperature at 700 ˚C under oxygen atmosphere at a flow rate of 500 ml/min. The sensors were demonstrated to be sensitive to various volatile organic compounds (VOCs), especially ethanol vapor. The E-nose even with only two sensors was efficient to discriminate a number of selected VOCs. The Au-doped sensor shows a significant improvement of sensitivity. The portable E-nose can detect the difference between alcohol beverages and alcohol solutions and can distinguish the difference of white and red wines having the same percentage of alcohol.

The pure and Au-doped ZnO nanostructure sensors were prepared using thermal oxidation technique. The oxidation was performed by heating zinc powder (purity 99.9%)

and a mixture of zinc powder and 10 wt% Au powder. Such mixtures were screened as a thick film onto an alumina substrate. The thick films were sintered at 700 °C for 24 hours under oxygen atmosphere with flow rate of 500 ml/min. The ZnO nanostructures were characterized using field emission scanning electron microscopy (FE-SEM). The FE-SEM images of ZnO and 10 % wt. of Au-doped ZnO nanostructure sensors on the alumina substrate are displayed in Fig. 1.

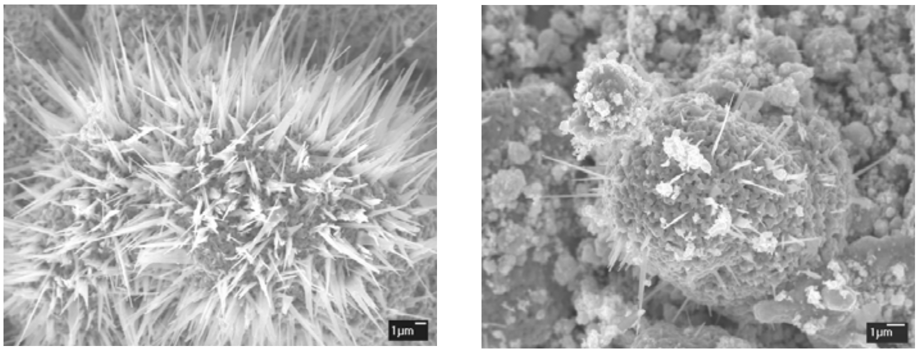


Fig. 1 FE-SEM image of (a) ZnO and (b) 10 % wt. of Au-doped ZnO nanostructure

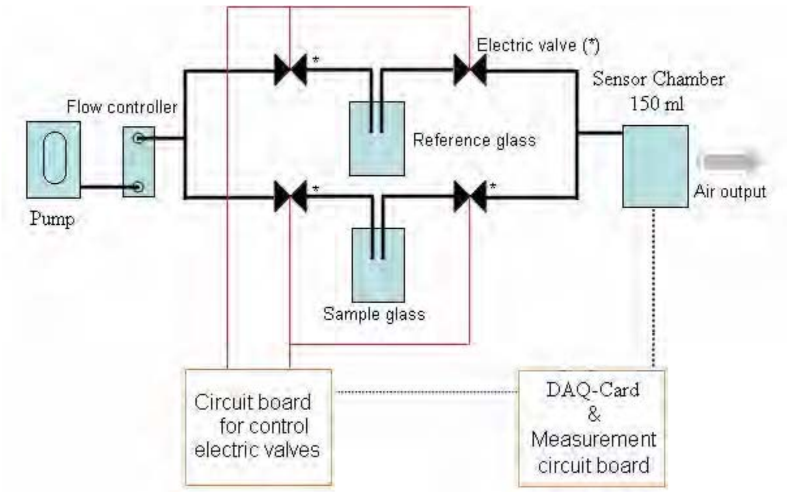
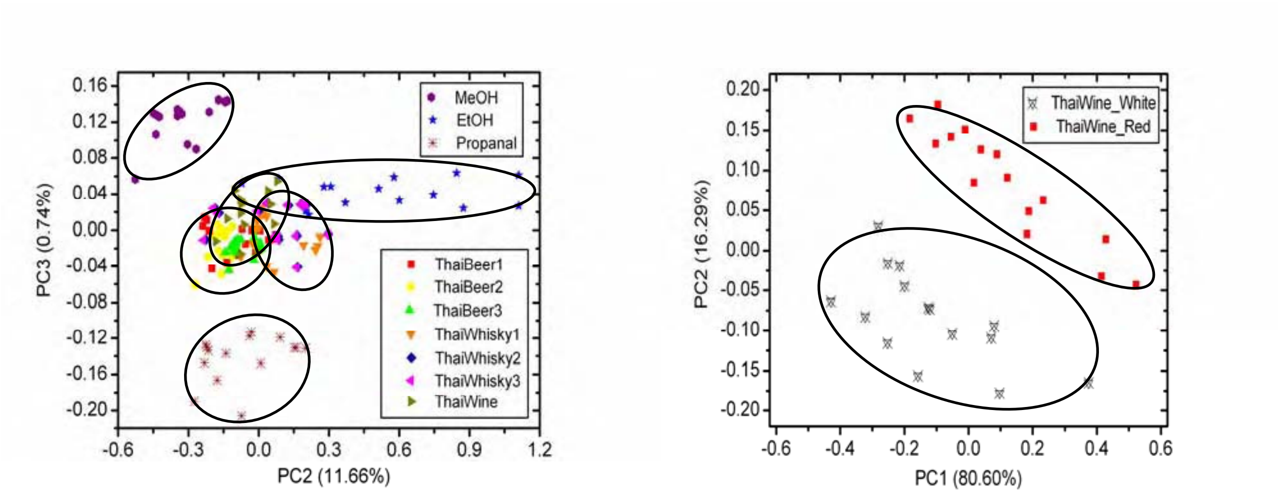


Fig. 2 Schematic diagram of dynamic portable E-nose system

The portable E-nose system (see Fig. 2) consists of three main parts: (i) sensor chamber (ii) air flow system and (iii) DAQ card & measurement circuit. All parts were contained in a rectangular box having a dimension of 19.5x29.5x10 cm3, respectively. For the first part, the two nanostructure sensors were installed at the bottom of the chamber. The air carrying the odor molecules was introduced into the 150 ml of sensor chamber through a Teflon tube. The caliber is about 2.5 mm. The sensor chamber also has an exhaust Teflon tube which has the same caliber. The second part consists of four electrically controlled solenoid valves, sample and reference glass containers, plastic pipes, and flow controller. It is necessary for this type of measurement to switch between a reference and a sample glass in order to reduce the humidity effects. Four electrically controlled solenoid valves were used to avoid mixing of the gas from the reference and the sample. Then, the gas from the reference or sample flows to the sensor chamber of which the flow rate was set at 2 L/min. Finally, in the measurement circuit, data acquisition was realized by a USB-DAQ-Card National Instruments NI USB-6008. The measurement program was written using LabVIEW.

The pure and 10 wt% Au-doped ZnO nanostructure sensors were successfully produced by using thermal oxidation technique. Doping 10 wt% of Au could improve the sensitivity of gas sensors on VOCs. The responses of the sensors are linear with gas concentrations varying from 100 to 1000 ppm. Therefore, it can be used for predicting the gas concentrations of unknown VOCs. In the real applications, only two sensors can be installed in the E-nose which is sufficiently efficient to detect and discriminate various different alcohol beverages. This E-nose can then be employed for quality control in the beverage industry. These elementary results are promising for further applications of this E-nose which can be further enhanced by using a higher number of ZnO sensors at various Au-doping percentages.

Because such sensors could well respond to alcohol. The ethanol, methanol, propanol and various Thai beer, Thai Wine and Thai whiskey samples were measured using the E-nose based on two nano-sensors. The data were introduced into the principle component analysis (PCA) for recognition and discrimination of samples. The PCA method can be used for dimensionality reduction of a dataset while retaining those characteristics of the dataset that contribute most to its variance. The input data can be the percentage change of every sensor or only some sensors for multiple measurements of different samples. However, in this E-nose, there are only two sensors. It means that the dataset only has two dimensions. Feature extraction techniques need to be applied to raw data for selecting the appropriate data and for increasing the dimension. The last 10 samples of each sensor before and after switching to another line were averaged. The difference of both values was used. Another feature can be extracted from the range of decay times. The difference of slope for the sample measurement was also used. Therefore, one experiment can give four different sensor output features.



(a) (b)

Fig. 3 PCA results for discriminate of (a) alcohols and (b) typical Thai wines

Fig. 3 shows 2D-PCA results for discrimination of alcohols. In Fig. 3, one can observe that the E-nose based on two nano-sensors can discriminate quite well between the ethanol, methanol and propanol with PC2 of 11.66 % and PC3 of 0.74 %. Thai alcoholic beverage sample points locate around the ethanol sample points because alcoholic beverages have the contents of ethanol. However, in case of Thai wines having the same percentage of alcohol (12.5% alcohol by volume), the E-nose can clearly discriminate the white and red wines as seen in 'Fig. 5b' with different PC1 of 80.60% and PC2 16.29%. The discrimination of white and red wines even with the same alcohol amount indicates that the E-nose is sensitive to other vapor ingredients apart from alcohols as well.

<u>Carbon Nanotube-Tin Oxide Sensors</u>

A portable electronic nose (E-nose) based on hybrid carbon nanotube-SnO2 gas sensors is described. The hybrid gas sensors were fabricated using electron beam (E-beam) evaporation by means of powder mixing. The instrument employs feature extraction techniques including integral and primary derivative, which leads to higher classification performance as compared to the classical features (R and R/R0). The results show that doping of carbon nanotube (CNT) improves the sensitivity of hybrid gas sensors, while quantity of CNT has a direct effect on selectivity to volatile organic compounds, i.e. MeOH and EtOH. The real-world applications of this E-nose were also presented. Based on the proposed methods, this instrument can monitor and classify 1% vol. of MeOH contamination in whiskeys.

The gas sensors were fabricated by electron beam (E-beam) evaporation. At first, Cr/Au interdigitated electrode was deposited on an alumina substrate. Prior to the deposition, the substrates were cleaned by oxygen-ion bombardment under a vacuum pressure of ~10−4 Torr in order to improve the adhesion of the film to the substrates. The width, spacing, and length of the interdigitated electrodes are approximately 100 μm, 100 μm, and 1 mm, respectively. Then, the compressed pure SnO2 and mixed CNT- SnO2 materials (i.e. 0.5 and 1 wt% CNTs) were E-beam evaporated over interdigitated electrode through another electroplated shadow mask with square window pattern aligned to the interdigitated area. The deposition rate and ion source parameters including ion driving voltage, and ion flux current were based on previous studies by A. Wisitsoraat et al. The film thickness of sensing materials is ~300 nm. The evaporated film was then annealed at 500 °C for 3 h. Finally, a NiCr (Ni 80% and Cr 20%) layer was also E-beam evaporated over the backside of substrate to perform as a heating unit. The NiCr heater can heat up to 350 °C.

An electronic nose (E-nose) has been developed in a form of briefcase (19.5x29.5x10 cm3). Figure 4 shows a schematic diagram indicating the key components of the portable E-nose system. The clean air produced from a pump carries aroma molecules of sample into sensor chamber at flow rate 2 L/min. Four electrical solenoid valves were used to avoid mixing of the gas from the reference and the sample. It is necessary for this type of measurement to switch between a reference and a sample glass in order to reduce the humidity effects.

The sensor array consisting of three gas sensors; SnO2, (0.5%) CNT-SnO2 and (1%) CNT-SnO2 was symmetrically embedded at the bottom of a Teflon chamber. A simple linear circuit, called as voltage divider, was employed for measuring the resistance of each gas sensor. The load resistance is 20 k   1% while resistance of each gas sensor without aroma molecules is in the range 20-40 k . The voltage input is 5 V. The data were collected every second in a laptop using data acquisition card (NI-DAQ 6008) and LabVIEW for subsequent analyses.

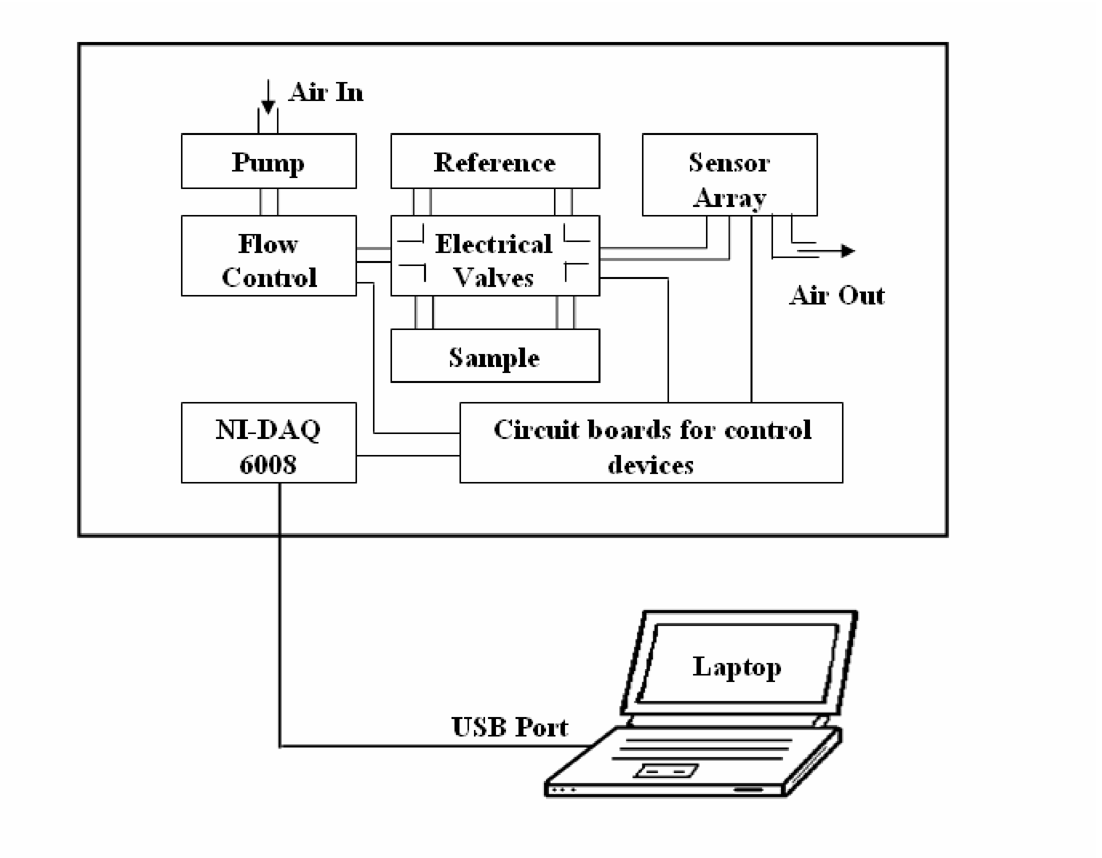


Fig. 4 Schematic diagram of portable electronic nose

We have reported the design, implementation and an example application of portable E-nose based on CNT-SnO2 gas sensors including new feature extraction methods for improvement of data classification. The doping of CNTs could enhance the sensitivity of SnO2 sensor while their concentration plays an important role in selectivity to volatile organic compounds such as EtOH and MeOH. The PCA results indicate that the newly proposed feature extraction including integral and primary derivative leads to higher classification performance as compared to the standard features (R and R/R0). The portable E-nose based on only two nanostructure sensors combined with proposed feature extraction methods shows clearly the classification of MeOH contamination mixed in the whiskey at higher concentrations than 1% by volume. It is hoped that such E-nose will be a useful tool for the whiskey industry and for quick screening of village-made whiskeys that are usually found of the MeOH contaminant.

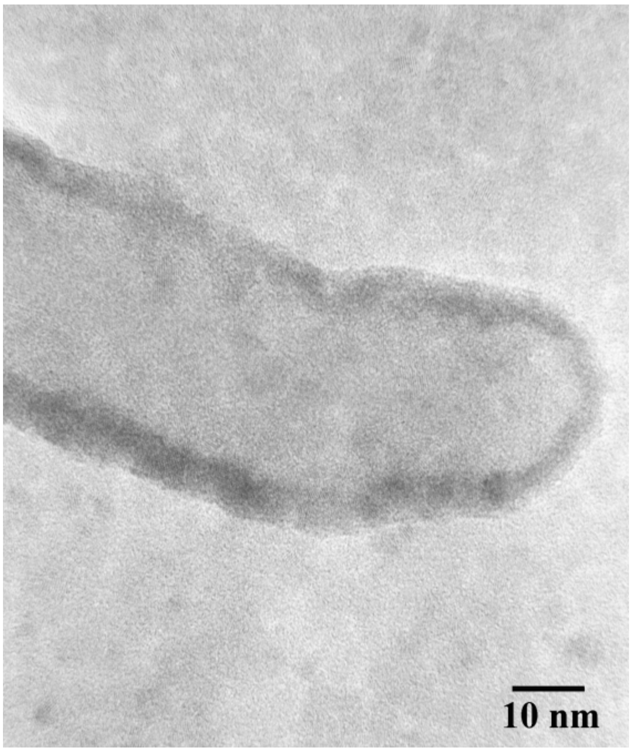


Fig. 5 TEM image of CNT-SnO2 film

The detailed structure of CNT-SnO2 composite was characterized by transmission electron microscope (TEM). TEM samples were prepared by E-beam evaporation of SnO2/CNT onto carbon coated copper TEM grid, which was done at the same time as coating on interdigitated electrodes. A typical HRTEM (High Resolution-TEM) image of CNT-SnO2 composite is shown in Fig. 5. From the TEM images, it can be identified that a single multi-walled CNT fragment is indeed embedded in nanocrystalline SnO2 layer. The diameter of CNTs and the crystal size of SnO2 are estimated to be in the range of ~20-40 nm and 3-10 nm, respectively.

The PCA results (Fig. 6) show that the feature extraction based on ΔR cannot classify the contamination of MeOH in whiskey due to the drift effect of sensor signal depending on temperature variation in the long time measurement. The classical relative response ($\Delta R/R_0$) seems to give a better result than ΔR but many samples disperse in the same region and pure whiskey results locate rather close to whiskey having 1 vol% of MeOH contamination while MeOH content exceeding 2% (v/v) would harm the consumer. In such case, the resolution power is not enough to guarantee the contamination of MeOH in whiskey. For feature extraction using both the integral and primary derivative data treatments, PCA results show a perfect classification between pure whiskey and whiskey having MeOH contamination. Moreover, the primary derivative can cluster all level of MeOH contaminations (1 vol%, 5 vol%, 10 vol% and 20 vol%) in the whiskey as shown in Fig. 6. The results indicate that the proposed feature extractions; integral and primary derivative, provide good capabilities in the recognition and discrimination of MeOH contamination. These may be alternative ways to replace the common methods (ΔR and $\Delta R/R_0$) which are widely used in PCA analysis.

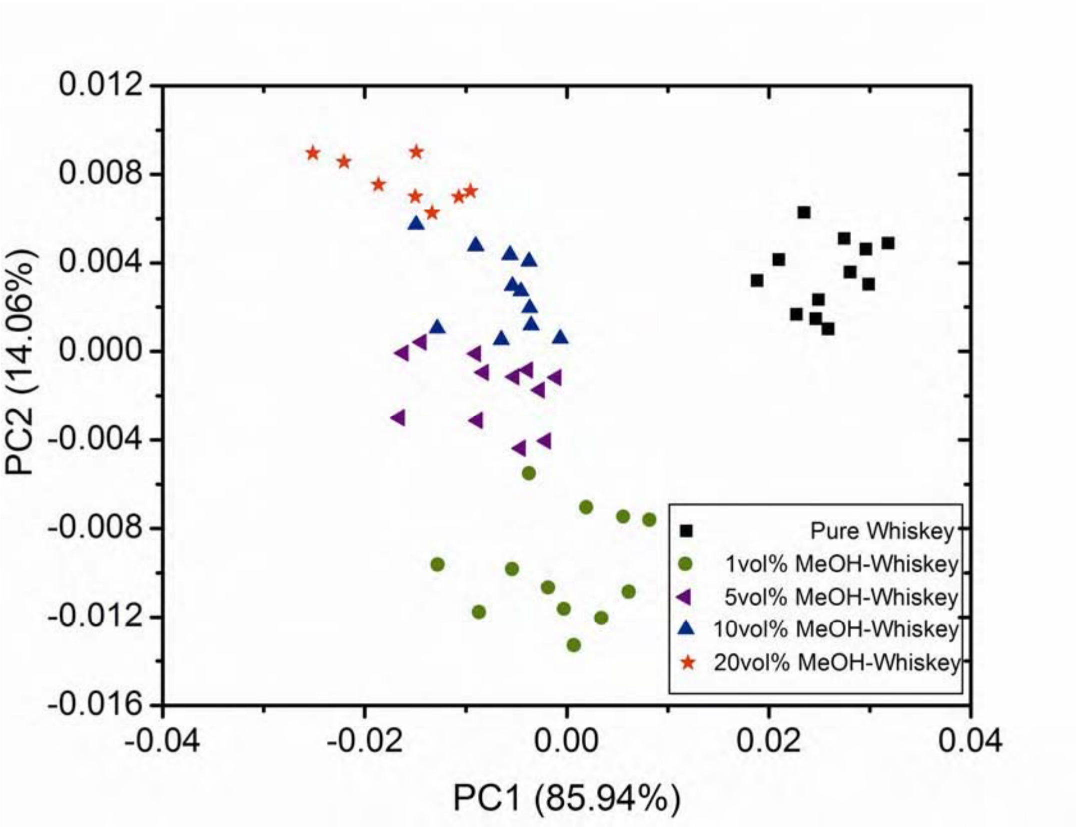


Fig. 6 PCA of pure and simulated contaminated whiskeys

From our PCA results together with feature extraction technique, it can be seen that although the sensors are structurally similar, they can have sufficiently distinct response such that it can be used to discriminate different kind of similar odors. However, it should be noted that features extracted from response behaviors can be dependent on some measuring details such as chamber size, gas flow rate, and sensor position in the sensor chamber. Consequently, the feature extraction result can be considerably different for different E-nose systems. Nevertheless, it should not be a problem for E-nose applications because this can be well controlled for each E-nose system and any E-nose system must always be trained under a fixed condition.

Carbon Nanotube-Tungsten Oxide Sensors

In this work we have fabricated hydrogen gas sensors based on undoped and 1 wt% multi-walled carbon nanotube (MWCNT)-doped tungsten oxide (WO3) thin films by means of the powder mixing and electron beam (E-beam) evaporation technique. Hydrogen sensing properties of the thin films have been investigated at different operating temperatures and gas concentrations ranging from 100 ppm to 50,000 ppm. The results indicate that the MWCNT-doped WO3 thin film exhibits high sensitivity and selectivity to hydrogen. Thus, MWCNT doping based on E-beam co-evaporation was shown to be an effective means of preparing hydrogen gas sensors with enhanced sensing and reduced operating temperatures. Creation of nanochannels and formation of p-n heterojunctions were proposed as the sensing mechanism underlying the enhanced hydrogen sensitivity of this hybridized gas sensor. To our best knowledge, this is the first report on a MWCNT-doped WO3 hydrogen sensor prepared by the E-beam method.

Commercial WO_3 powder was obtained from Merck and used without further purification. MWCNTs were grown by the thermal chemical vapor deposition (CVD) process. The catalyst layer of aluminium oxide (10 nm) and stainless steel (5 nm) was deposited on the silicon (100) substrates (Semiconductor Wafer Inc.) using reactive sputtering apparatus. The synthesis of MWCNTs was performed under a flow of acetylene/hydrogen at a ratio of 3.6:1 at 700 °C for 3 min. To obtain high-purity MWCNTs, the water-assisted selective etching technique [28] was applied after each CNT's growth stage. Water vapor (300 ppm) was introduced into the system by bubbling argon gas through liquid water at room temperature for 3 min. The sequence of acetylene/hydrogen and water vapor flows was repeated for five cycles. Based on the scanning electron microscopic (SEM) image, as shown in Figure 1, the diameter and length of the MWCNTs are ~35 nm and ~26 µm, respectively. The electrical conductivity of MWCNTs was ~75 S/cm, as measured by a four-point probe method at room temperature. In addition, high-resolution transmission electron microscopic (HR-TEM) imaging confirms that CNTs are multi-walled, with the width and number of walls being ~4.6 nm and 14, respectively. Thus, the spacing between two graphitic layers is ~0.33 nm, which is in good agreement with theoretical and experimental values.

MWCNT-doped WO3 thin film was fabricated by the E-beam evaporation technique onto Cr/Au interdigitated electrodes on an alumina substrate. The target was prepared by mixing 99 wt% of WO3 powder with 1 wt% of MWCNT powder using a grinder in a mortar for 30 min and then pelletizing with a hydraulic compressor. Deposition was performed at a pressure of 5 × 10−6 Torr in the evaporation chamber. The substrate was rotated and kept at 130 °C during the deposition in order to obtain a homogeneous thin film. The deposition rate was 2 Å/sec and the final film thickness was 150 nm, as controlled by a quartz crystal monitor. After E-beam evaporation, the film was annealed at 500 °C for 3 h in air to stabilize the crystalline structure. In addition, an undoped WO3 thin film was also fabricated using the same conditions for comparison.

To evaluate the gas sensing properties of the thus prepared thin films, MWCNT-doped WO3 and undoped WO3 gas sensors were placed inside a stainless steel chamber and the resistance measured using a 8846A Fluke multimeter with 6.5 digit resolution. The gas sensing measurements were made within a dynamic flow system with control of sensor operating temperatures (200–400 °C) under variable gas concentrations (100–50,000 ppm). Hydrogen (H2), ethanol (C2H5OH), methane (CH4), acetylene (C2H2), and ethylene (C2H4) were used to test the sensing properties and selectivity of the thin films. The sample gas flow time and the clean air reference flow time were fixed at 5 min and 15 min, respectively. It should be noted that these switching interval was selected so that the resistance change is at least 90% of the saturated value. The sensor resistances were sampled and recorded every second using LabVIEW with a USB DAQ device for subsequent analyses.

Surface morphology, particle size and crystalline structure of the films were characterized by SEM and TEM. Figure 7 shows the SEM surface morphology of MWCNT-doped WO3 thin film deposited on an alumina substrate. It was seen that the film coated on the rough alumina substrate has approximate grain sizes ranging from 40 to 80 nm. The nanometer grain size together with the roughness of the alumina substrate can enhance the gas sensitivity of thin films because more gas adsorption sites are available due to the increased surface area and porosity. With the SEM resolution, CNT structure cannot be observed on the thin film surface. Therefore, TEM characterization was used to confirm CNT inclusion into the WO_3 film. It should be noted that copper TEM grid samples were loaded inside the evaporation chamber for sample deposition at the same time as coating on the Cr/Au interdigitated electrodes. TEM observation clearly shows

CNT inclusion into the nanocrystalline WO_3, while the electron diffraction pattern exhibits polycrystalline phase in the film, as shown in Figure 8a,b, respectively.

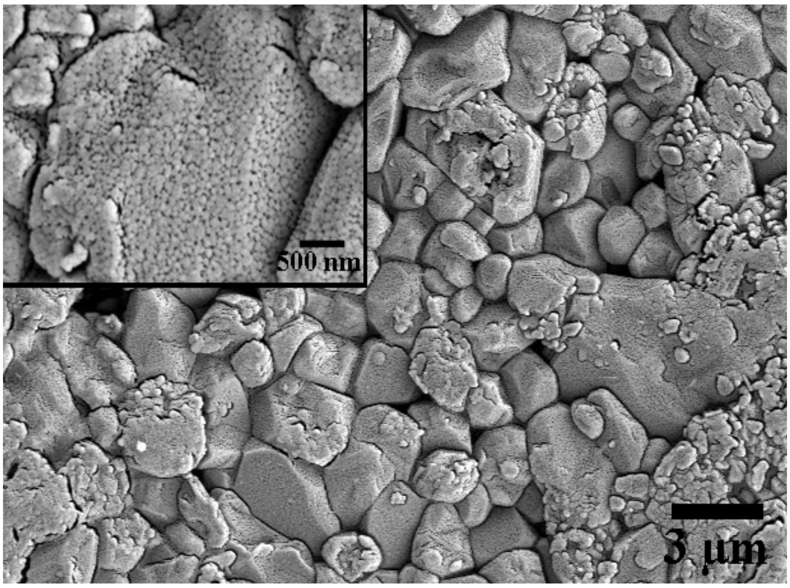
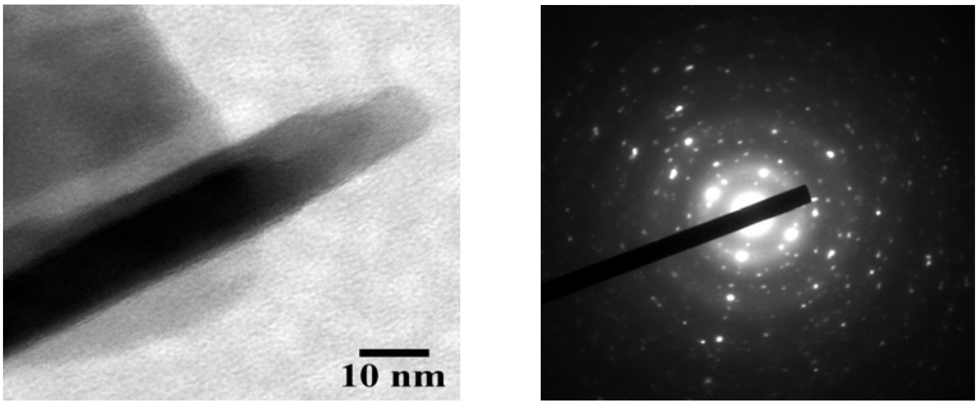


Fig 7. SEM image of MWCNT-doped WO_3 thin films on alumina substrate.



(a) (b)

Fig. 8 (a) High-resolution TEM image and (b) corresponding selected area diffraction pattern of MWCNT-doped WO_3 thin film.

The film morphology obtained in our study is in accordance with observations on nanocrystalline WO3 films grown by other methods. Doping of CNT does not change the phase or surface morphology of the film, but it may help form nanochannels in WO3 films, leading to the enhancement of the sensitivity and reduction of the operating temperature.

One major advantage of MWCNT-doped WO3 thin film is that the sensor can be operated at a lower operating temperature (250 °C), especially if this sensor is used to measure the H2 gas at higher concentrations (5,000–50,000 ppm). As shown in Figure 9, at such a concentration range, there are sufficient numbers of H2 molecules available to react with the surface oxygen adsorption sites. It is also well-known that MWCNTs contribute to the reduction of sensor resistance of metal oxides and the activation energy between the WO3 surface and H2 gas.

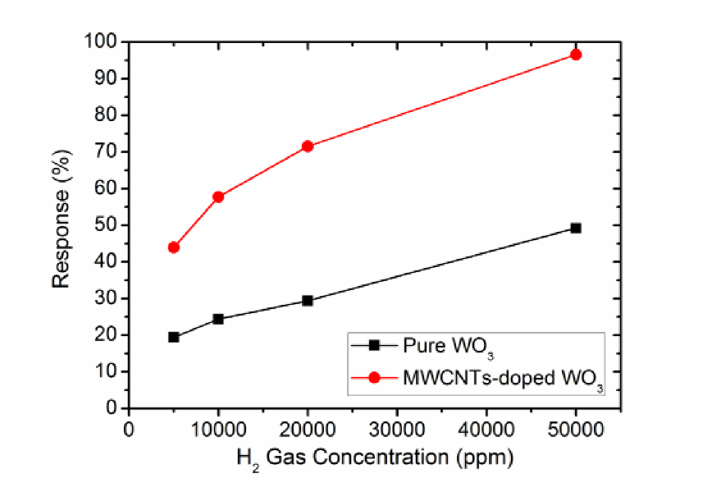


Fig. 9 Sensing response of the undoped WO3 and MWCNT-doped WO3 thin films to high H2 concentrations (5,000–50,000 ppm) at the operating temperature of 250 °C.

Polymer/Carbon Nanotube Nanocomposite Sensors

An electronic nose (e-nose) system based on polymer/carboxylic-functionalized single-walled carbon nanotubes (SWNT-COOH) was developed for sensing various volatile amines. The SWNT-COOH dispersed in the matrix of different polymers; namely, polyvinyl chloride (PVC), cumene terminated polystyrene-co-maleic anhydride (cumene-PSMA), poly(styrene-co-maleic acid) partial isobutyl/methyl mixed ester (PSE), and polyvinylpyrrolidon (PVP), were deposited on interdigitated gold electrodes to make the gas sensors. The response of these sensors to volatile amines was studied by both static and dynamic flow measurements. It was found that all sensors exhibited behaviors corresponding to Plateau–Bretano–Stevens law (R2 = 0.81 to 0.99) as the response to volatile amines. Real-world application was demonstrated by applying this e-nose to monitor the odor of sun-dried snakeskin gourami that was pre-processed by salting-preservation. This electronic nose can discriminate sun-dried fish odors with different stored days using a simple pattern recognition based on the principal component analysis (PCA).

Volatile amines are presented with strong and characteristic odor, mostly realized as unpleasant and toxic, i.e., the smell of ammonia, dried fish, putrid flesh and urine, etc. Amines are produced by decomposition of amino acids in biological processes. Therefore, amine sensor can be used to assess the freshness of protein-containing foods as well as contaminated environment[8] related to biological wastes. Spoiling fish typically generates several kinds of amines such as ammonia, trimethylamine (TMA), dimethylamine (DMA) (these volatile compounds are also known as Total Volatile Basic Nitrogen (TVB-N)) and histamine (biogenic amines).

Nowadays electronic nose has become a well-known technology for quality assessment of foods or drinks. Electronic nose (e-nose) is fast, portable, low-cost and reliable. In principles, an e-nose consists of an array of gas sensors working cooperatively to detect a wide range of gases. The sensor response patterns are then recognized in order to identify or discriminate specific odors. Gas sensors based on carbon nanotubes (CNT)/polymer composites measure the electrical response under room temperature. The nanocomposited CNT with various polymers have been demonstrated to detect selective gases at low concentrations.

In this work, we have developed a new electronic nose system for amine detection based on an array of polymer/CNT nanocomposite gas sensors. In general, the underlying mechanism of polymer/carbon nanotube gas sensors is based on percolation of analytic gases into the polymer matrix leading to a drop in electrical conductance caused by volumetric increase in the materials. In principles, the polymers used in this type of gas sensors are non-conducting. Therefore, carbon nanotubes are mixed into the polymer matrix to act as conducting channel. Diffusion of the analytic gases into the polymer increases the separation between the conducting channels, thus decreasing the conductivity of the materials. Based on the above-mentioned sensing principles, there are two major factors that control the sensitivity of this type of sensors; swelling capability of polymer and electron-donating capability of analytic gases into carbon nanotubes. Identification of amine molecules is performed by presenting a variety of polymeric matrices with non-specific chemical interactions in the sensor array combined with a simple pattern recognize algorithm such as principal component analysis (PCA).

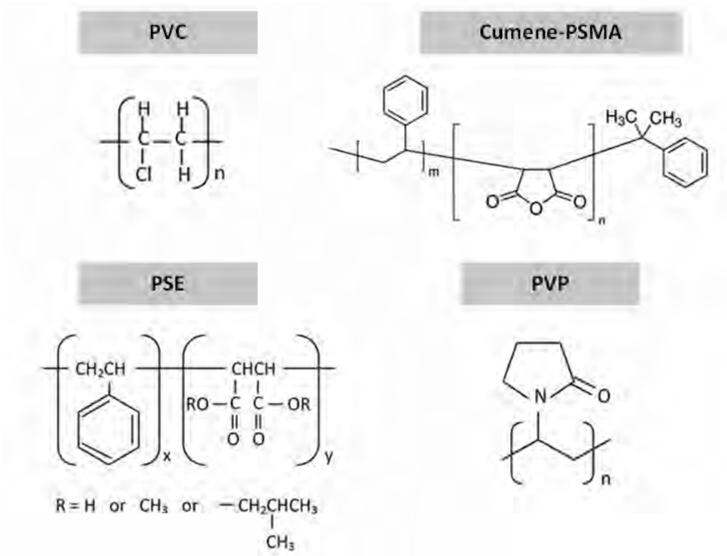


Fig. 10. Structures of polyvinyl chloride (PVC), cumene terminated polystyrene-co-maleic anhydride (cumene-PSMA), poly(styrene-co-maleic acid) partial isobutyl/methyl mixed ester (PSE), and polyvinylpyrrolidon (PVP).

The carboxylic-functionalized single-walled carbon nanotube (SWNT-COOH) was used for producing the composites because it can be easily dispersed in solvents or polymer matrix due to its polarity16-17. Higher degree of mixing as present in the functionalized CNT/polymer sensors leads to increasing response and reversibility beyond the pristine CNT/polymer composites.18-19 The purified SWNT-COOH (90wt%) with 1-2 nm in diameter and 0.5-2.0 μm in length obtained from Cheap Tube Inc (www.cheaptubesinc.com) was dispersed in the polymer solutions of (i) PVC, (ii) cumene-PSMA, (iii) PSE and (iv) PVP (structures shown in Fig. 10). Each polymer was dissolved completely in 1 ml of the proper solvent (tetrahydrofuran, acetone, acetone and water, respectively). By optimizing the resulted device resistances to a kilo-ohms range, SWNT-COOH loading about 10-30 wt% with respect to the polymer content was blended into polymer solution and placed in the ultrasonic bath for 15 min to obtain uniform composite. Nanocomposite materials were deposited onto interdigitated electrodes by spin-coating and heated at 150 oC for 1 h to remove the residual solvent and impurities. The interdigitated electrodes were fabricated by E-beam evaporation of Cr/Au over alumina substrates through electroplated-Ni shadow masks. The thickness of Cr and Au layers are ~50 nm and ~200 nm, respectively. The width, spacing, and length of the IDE are approximately 100 μm, 100 μm, and 1 mm, respectively.

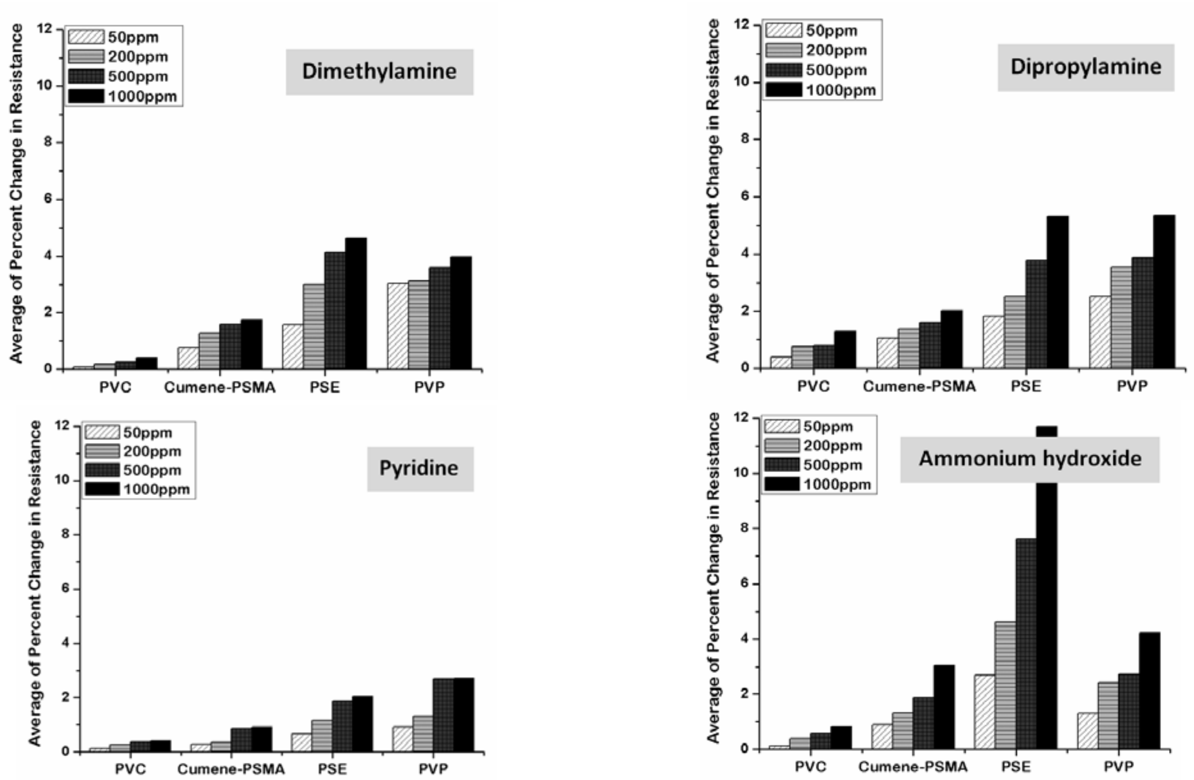


Fig. 11. The average of percent change in resistance of each sensor in static condition when exposed to dimethylamine, dipropylamine, pyridine, and ammonium hydroxide at the concentrations of 50-1000 ppm.

Fig. 11 plots the average percent change in resistance of the four sensors as exposed to dimethylamine dipropylamine, pyridine, and ammonium hydroxide under the static condition. It was found that the sensor response increases with the rising amine concentration. The power law in Eq.1 was used to model this behavior and the results can then be simplified as given in Table 1. The R-square (R^2) values of all sensors exceed the value of 0.81, which demonstrates that the Plateau–Bretano–Stevens law can be valid for all elements, especially for PVC/SWNT-COOH sensor response to dimethylamine (R^2=0.99). All sensors correspond to the exponent n < 1; therefore, the exponent is compressive and the sensor response increases slowly as the concentration increases.

According to the results, it was shown that PSE/SWNT-COOH composite gas sensor yields the highest response to amine volatile compounds. The underlying mechanism of this type of sensors requires that the analytic gas must diffuse into the polymer matrix via some types of molecular interactions. In most cases, the analytic gases interact weakly with the polymer through physi-sorption (i.e. dipole-dipole or van der Waals interactions). Specifically, the molecular structure of PSE allows stronger interactions (such as chemi-sorption) with amine compounds through the ester and carboxylic groups, as shown in Fig. 10. The strength of these interactions depends on the basicity of the amine compounds (dipropylamine (pKb=3.09) > dimethylamine (pKb=3.29) > ammonia (pKb=4.75) > pyridine (pKb=8.75)). Because dipropylamine presents the highest basicity among other amines, it seems at first glance that this compound should exhibit highest sensing response with PSE. However, these secondary amines (dipropylamine and dimethyl amine) as well as pyridine have much lower mobility than ammonia to diffuse into the polymer matrix. As a result, the sensitivity of PSE to the amines is ranked as ammonia > dipropylamine > dimethylamine > pyridine), which is an outcome of the counterbalance between basicity and mobility of the volatile amines.

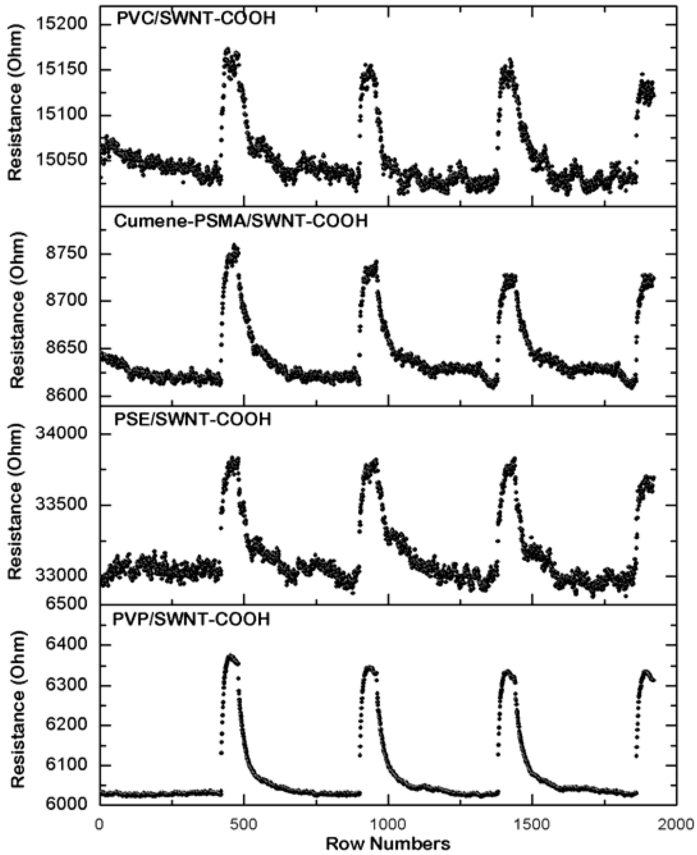


Fig. 12. The typical resistance changes with time of four sensors to sun-dried fish odor

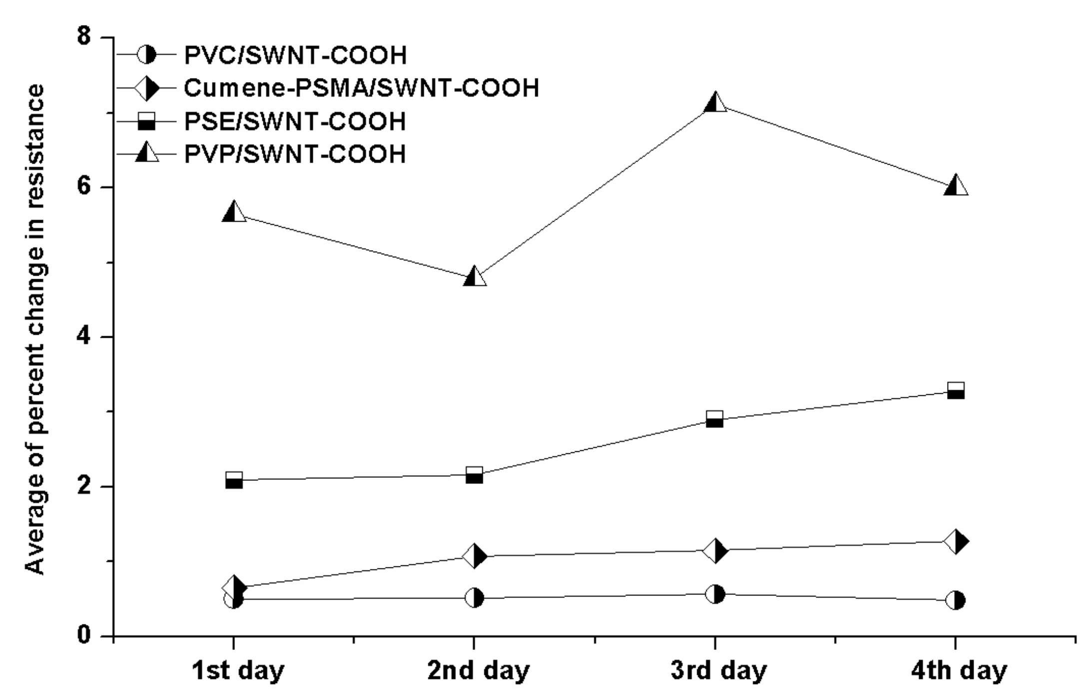


Fig. 13. The average of percent change in resistance of each sensor to volatile of the sun-dried snakeskin gourami between 1 to 4 days.

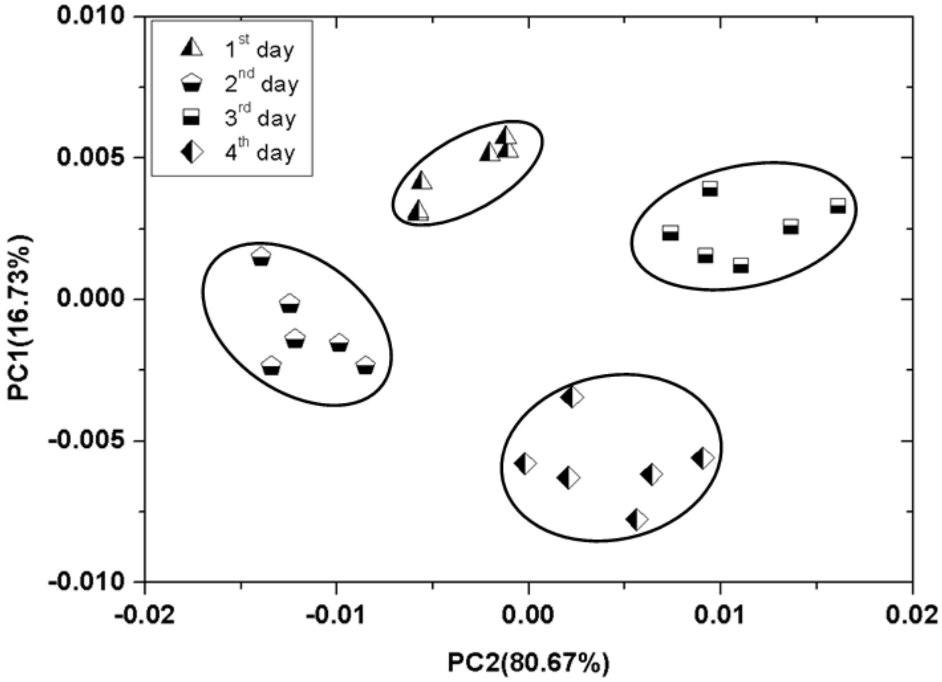


Fig. 14. The score plot of PCA for the sun-dried snakeskin gourami between 1 to 4 days.

Different capability of each polymer to swell the amine vapors leads to different sensitivity to each gas. Another factor that effects on the sensitivity is electron-donating properties of amine species to carbon nanotubes. Thus, the results indicate that the SWNT-COOH based on these polymers is a p-type semiconductor. In principles, e-nose should be made from an array of gas sensors that have different selective gases. By measuring a complex odor such as the sundried snakeskin gourami, pattern recognition is required to understand the data obtained from the measurement. Fig. 12 shows the response of each sensor to the odor of the fish samples. A reversible behavior was observed in all sensors. A major obstacle for polymer composite gas sensors is well recognized as their poor stability. The efficiency of such sensors often decreases after repetitive usages. Moreover, thick sensing film may confine adsorbed volatile molecules within the polymer matrix. Therefore, optimization of the flow rate and measurement time must be optimized in order to maintain the consistency of the extracted features.

Fig. 14 plots the sensor responses to the fish sample at different storage days (1 - 4 days). The increasing response from the 1^{st} to 4^{th} day indicates increasing amine vapors in the sample during that period. The principal component analysis of these data was performed and plotted in Fig. 8. The PCA results show 80.67% and 16.73% of variance within the first and second components (PC1 and PC2) which implies that visualization of these data on 2D plot is highly relevant and e-nose made of these 4 sensors is sufficient to discriminate these samples. Data analysis by PCA can identify 4 groups of data based on their storage time (1 to 4 days).

Metallo-Porphyrins Optical Sensors

Metal porphyrins (MP) are organic semiconductor materials able to adsorb gas molecule at the central metal atom or on the conjugated ¶-electron circumference. The electrical and optical properties of MP are strongly induced by electron donors and acceptors. As a result, MP has become a versatile material for gas sensor because many transducing techniques are allowed such as electrical, optical and mass transduction. In particular, the MP-based optical sensors provide many advantages over metal oxide-based sensors. Optical transducing is a rather convenient measurement method which may be operated at room temperature. Optical absorption spectra also yield much more informative and specific results with regards to chemical types than chemoresistive sensors. Only a single type of MP materials can be applied to make a device that can behave as an array of sensors. We have previously shown that MgTPP and ZnTPP thin films can detect various volatile organic compounds (VOCs) based on UV-Vis spectroscopy. In this work, we demonstrate the potentials of these sensor materials for an artificial nose system aimed at the beverage industry.

In this work, the spin-coating technique was employed to fabricate MgTPP and ZnTPP thin films, followed by X-ray diffraction (XRD) and atomic force microscopy to investigate the microstructure of the films. An artificial nose based on optical absorption change was constructed by housing the films in a flow chamber installed in between the light source and the detector probe of a UV-Vis spectrophotometer. The sensing properties were tested with various VOCs, namely, alcohols, acetone (5% aq.), acetic acid (5% aq.), methyl benzoate (5% aq.), and commercial alcoholic beverages. Theoretical calculations based on the density functional theory (DFT) were used to provide the understanding of VOCs-sensor interactions.

A pattern recognition technique based on the principal component analysis (PCA) has been demonstrated to classify many odors, such as alcohols, octane, toluene, and methylethylketon in the artificial noses. In addition, PCA was successfully used in colorimetric sensor array to describe the soft drinks and portable E-nose based on CNT–

SnO2 gas sensors to describe the contamination of methanol in whisky. To demonstrate the discrimination power of the MgTPP and ZnTPP thin films and the corresponding electronic nose, PCA has been employed to explore the data distribution and classify the samples.

MgTPP and ZnTPP were obtained from Sigma-Aldrich and Silpakorn University (synthesized by Dr. Radchada Buntem), respectively. MgTPP and ZnTPP were dissolved in chloroform at concentration of 0.017 M and 0.007 M, respectively. The solutions were subsequently spin-coated onto glass substrates at 1000 rpm for 30 seconds. A previous work has shown that improvements in the MgTPP gas sensing properties could be achieved by thermal annealing. Therefore, MgTPP spin-coated thin films were placed in a furnace under the argon atmosphere, heated at the rate of 5 °C per minute to reach 280 °C and then allowed to cool down for 3 hours. The optical absorption spectra of thin films were recorded at the normal incidence in the range of 300-800 nm by the Jenway UV-Vis Spectrophotometer.

The gas sensing capability of the metal-tetra phenyl-porphyrin films have been investigated under the dynamic gas flow through a home built stainless steel chamber, equipped with quartz windows for optical measurements. Nitrogen (99.9%) gas was used as the reference and carrier gas to conduct headspace vapor from the sample bottle. The sample bottle was immersed in a heat bath controlled at 25 °C. The gas flow was switched between the reference and the vapor sample every 10 minutes. The measurements of each VOC consist of 5 alternating cycles between the reference and the sample. The experiment was repeated for at least another two times on each VOC.

The absorption spectra of the MgTPP films were signified by the intense B band and Q band, as shown in Fig. 15. MgTPP exhibits the B band peak at 438 nm and the Q band peaks at 570 and 610 nm. After thermal annealing, the B band intensity became lowered. In the case of ZnTPP, the B band peak at 436 nm and the Q band peaks at 555 and 600 nm are observed and the total absorbance also decreased after thermal annealing. The annealing process should therefore produce similar structural changes in both MgTPP and ZnTPP films, which has been explained to be a result of thermally-induced crystallization. However, our previous study found that the annealing process the annealed MgTPP films yielded higher responses to methanol vapor than the as spin-coated films, whereas the spin-coated ZnTPP films presented stronger methanol response than the treated films. So in this work, we compared the gas sensing properties between annealed MgTPP films and as spin-coated ZnTPP films.

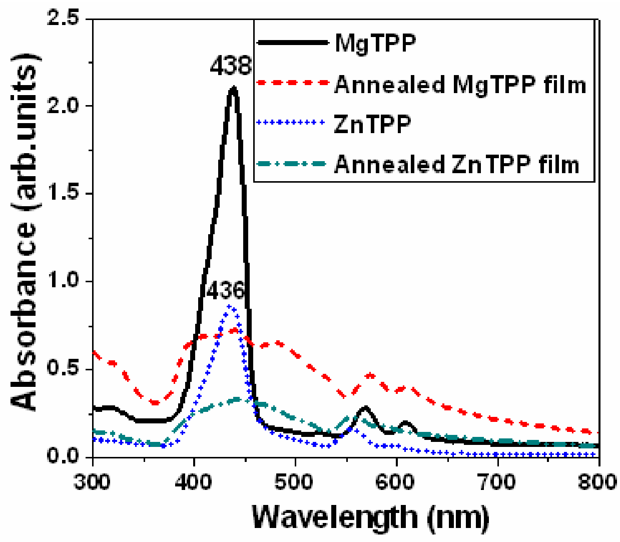


Fig. 15. Optical absorption spectra of the MgTPP and ZnTPP thin films.

Fig. 16 shows the average gas sensing of MgTPP and ZnTPP film to 10 mol% of alcohol vapor in nitrogen gas. Both MgTPP and ZnTPP films express more sensing response to methanol than other alcohols. It can be seen that MgTPP is more selective to methanol comparing to ZnTPP. Thus, ZnTPP expresses higher response to ethanol and isopropyl alcohol than MgTPP. In Fig. 16, the treated MgTPP films showed the molecular crystallization and the increasing of the grain size. The average roughness for MgTPP spin-coated film was about 2.83 nm. After thermal treatments, the MgTPP grain size can be approximated from the roughness to be 41.7 nm and the grain sizes of the treated MgTPP films is larger than ZnTPP spin coated film, showing the average roughness about 15 nm. The thickness of MgTPP and ZnTPP films are approximately 200 and 170 nm, respectively. Furthermore, in Fig. 3, the as spin-coated ZnTPP film shows stronger responses than MgTPP in Region 2 for all VOCs. The strongest response for both porphyrin sensors corresponds to the Soret band which is located at 438 and 436 nm, indicating the pi-pi* transition between bonding and anti-bonding molecular orbital in porphyrin compound.

The structure of porphyrins powder and film were investigated by XRD (Cu Kα radiation, λ=1.5418 nm) as shown in Fig. 17. The intensity peaks at 2θ equal to 11^{o} and 13^{o} for all films are the effect of the glass slide substrate. For MgTPP, the diffraction peak of the annealed film occurs at 18.7^{o}, which is absent in the non-annealed film. This peak corresponds to an interplanar distance (*d*) of 4.73 nm. This peak is also related to the main peak of MgTPP powder located at 18.3^{o}. For ZnTPP, there is the diffraction peaks of both spin coated and annealed films. The diffraction peaks of spin coated film are observed at 7.2^o and 18.5^o and the diffraction peaks of annealed film shift to 7.3^o and 18.6^o, which corresponds to an interplanar distance (d) of 12.07 and 4.76 nm, respectively. In addition, the absorption spectra shifts of annealed MgTPP and ZnTPP films in Fig. 15 were explained by an increase in diffraction peak intensities after thermal annealing.

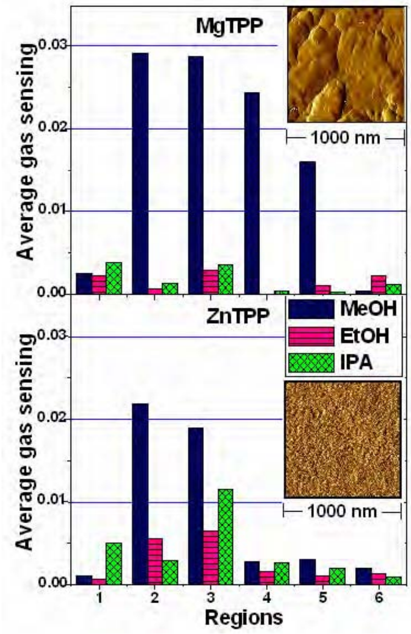


Fig. 16. The average gas sensing and DFM images in top views of MgTPP annealed film and ZnTPP spin coated film.

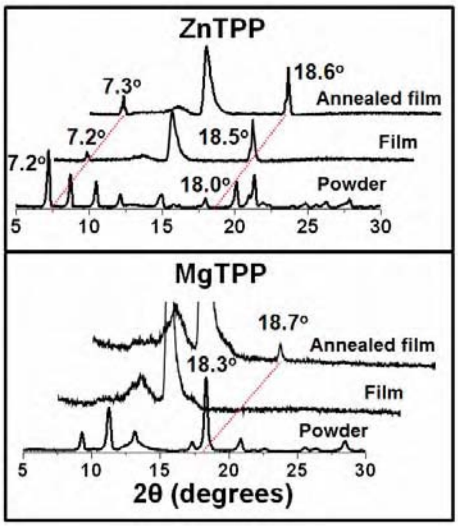


Fig. 17. The XRD patterns of MgTPP and ZnTPP compounds.

DFT was used to predict and explain the gas-sensing characteristic of the organic compound. The lowest interaction energies from calculation method indicated that MPs present the stable structure with VOCs molecule in the optimized site. The interaction energies and the change in HOMO-LUMO energy gap of MTPP with one VOC molecule and two VOC molecules in Table 1 indicate that MTPP have the high interaction energies and the higher change in energy gap when it interacts with 1 VOC molecule. Both optical gas sensors indicated the strongest interactions with methanol, about -9.92 kcal/mol and -5.79 kcal/mol for MgTPP and ZnTPP, respectively. This computational result agrees with the experiment results which measured alcohol sensing at the same molar concentration. Amongst ethanol, methanol and iso-propanol, both the MgTPP and ZnTPP films exhibit the strongest optochemical responses to methanol. This seems to be in accordance with the trends in the interaction energies and the NBO charge transfer. The interaction of porphyrin film with VOC gas is determined by the metal atom site via the interaction of the π electrons and the free electrons of the metal atom in porphyrin with the electrons of a gas molecule. Therefore, electron transfer from the metal atom in porphyrin to an oxygen atom of the VOC molecule occurs when MgTPP/ZnTPP are in contact with the VOC molecule. The interaction energy at this site depends on the chemical properties of the central metal atom, such as electro-negativity and spin state.

Overall, the DFT calculations show a clear difference of the molecular interaction nature with VOC between MgTPP and ZnTPP. The annealed MgTPP shows higher responses to methanol than the as spin-coated ZnTPP films in both experimental and computational results. In addition, the annealed MgTPP film with a micro-crystalline structure, as evident from the AFM and XRD results, produces higher methanol response than the as spin-coated MgTPP films, whereas the opposite trend has been observed for ZnTPP. In general, strong gas-sensing response is to be expected from films with smaller grain sizes because of a higher surface area. The result of the MgTPP films seems initially to contradict the common sense. However, since the interactions of porphyrin and VOC molecules should occur via the charge transfer process. On one porphyrin semiconductive micro-crystal, one interacting VOC molecule can induce optical absorption change to the whole crystal, which may lead to the enhanced sensitivity. Meanwhile, for the ZnTPP, the as spin-coated films exhibit a better sensitivity. This may be possibly explained by structural changes induced by solvent vapor, which has been observed in the case of zinc phthalocyanine.

MgTPP and ZnTPP spin coated thin films have been fabricated as optical gas sensors and applied to classify many types of VOCs under an artificial nose setup. The sensing response of the porphyrin molecules to vapor molecules was monitored by changes in the optical absorbance. MgTPP and ZnTPP thin films presented strong sensing signals with methanol and Thai whisky, respectively. In addition, the computational results were compared with experiment results, which confirm that, amongst methanol, ethanol and iso-propanol, MgTPP yields the highest interaction energy with methanol at the same concentration of alcohol vapor. XRD confirms that crystallization enhanced by thermal annealing of the MgTPP film helps improve the sensing response. Based on the PCA pattern recognition technique, both MgTPP and ZnTPP films can be successfully applied to discriminate three types of alcohols and Thai beverages.

5. OUTPUT FROM THIS PROJECT

PUBLICATION

(1) Chatchawal Wongchoosuk, Supab Choopun, Adisorn Tuantranont, Teerakiat Kerdcharoen, "Au-doped Zinc Oxide Nanostructure Sensors for Detection and Discrimination of Volatile Organic Compounds", *Materials Research Innovation* 2009, vol. 13, pp. 185-188.

(2) Chatchawal Wongchoosuk, Mario Lutz and Teerakiat Kerdcharoen, "Detection and Classification of Human Body Odor Using an Electronic Nose", *Sensors* 2009, vol. 9, pp. 7234-7249.

(3) Chatchawal Wongchoosuk, Anurat Wisitsoraat, Adisorn Tuantranont, Teerakiat Kerdcharoen, "Portable Electronic Nose Based on Carbon Nanotube-SnO2 Gas Sensors and Its Application for Detection of Methanol Contamination in Whiskeys", Sensors and Actuators B 147 (2010) 392.

(4) Chatchawal Wongchoosuk, Anurat Wisitsoraat, Ditsayut Phokharatkul, Adisorn Tuantranont and Teerakiat Kerdcharoen, "Multi-walled Carbon Nanotubes Doped Tungsten Oxide Thin Film for Hydrogen Gas Sensing", Sensors 10 (2010) 7705 .

(5) Panida Lorwongtragool, Anurat Wisitsoraat and Teerakiat Kerdcharoen, "An Electronic Nose for Amine Detection Based on Polymer/SWNT-COOH Nanocomposite", Journal of Nanoscience and Nanotechnology (2011) in press.

(6) Sumana Kladsomboon, Sirapat Pratontep, Theeraporn Puntheeranurak, Teerakiat Kerdcharoen. "An Artificial Nose Based on M-Porphyrin (M = Mg, Zn) Thin Film and Optical Spectroscopy", Journal of Nanoscience and Nanotechnology (2011) in press.

PROCEEDINGS

(1) Panida Lorwongtragool, Chatchawal Wongchoosuk, Teerakiat Kerdcharoen, "Portable Electronic Nose for Beverage Quality Assessment", ECTI-CON2011 - 8th International Conference of Electrical Engineering/Electronics, Computer,

Telecommunications and Information Technology Association, 17-19 May 2011, Khon Kaen, THAILAND. (Indexed in SCOPUS and IEEE Explore Database)

(2) P. Lorwongtragool, C. Wongchoosuk, T. Kerdcharoen, “Portable artificial nose system for assessing air quality in swine buildings”, ECTI-CON2010 - 7th International Conference of Electrical Engineering/Electronics, Computer, Telecommunications and Information Technology Association, 19-21 May 2010, Chiang Mai, THAILAND. (Indexed in IEEE Explore Database)

(3) Weerayut Srichaisiriwech, Anurat Wisitsoaat, Ditsayut Phokharatkul, Chanpen Karuwan, Adisorn Tuantranont and Teerakiat Kerdcharoen, “Electronic Tongue Based on Modified Carbon Nanotube Electrochemical Sensor Array”, ECTI-CON2010 - 7th International Conference of Electrical Engineering/Electronics, Computer, Telecommunications and Information Technology Association, 19-21 May 2010, Chiang Mai, THAILAND. (Indexed in IEEE Explore Database)

(4) Panida Lorwongtragool, Anurat Wisitsoraat and Teerakiat Kerdcharoen, “An Electronic Nose for Amine Detection Based on Polymer/SWNT-COOH Nanocomposites”, IEEE International Nanoelectronics Conference (IEEE-INEC 2010), 4-7 January 2010, City University of Hong Kong, Hong Kong, CHINA. (Indexed in SCOPUS, IEEE Explore Database)

(5) Sumana Kladsomboon, Theeraporn Puntheeranurak, Sirapat Pratontep and Teerakiat Kerdcharoen, “An Artificial Nose Based on M-Porphyrin (M = Mg, Zn) Thin Film and Optical Spectroscopy”, IEEE International Nanoelectronics Conference (IEEE-INEC 2010), 4-7 January 2010, City University of Hong Kong, Hong Kong, CHINA. (Indexed in SCOPUS, IEEE Explore Database).

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(7) Sumana Kladsomboon, Sirapat Pratontep, Teerakiat Kerdcharoen, “Optical Electronic Nose Based on Porphyrin and Phthalocyanine thin films”, ECTI-CON2010 - 7th International Conference of Electrical Engineering/Electronics, Computer, Telecommunications and Information Technology Association, 19-21 May 2010, Chiang Mai, THAILAND. (Indexed in SCOPUS, IEEE Explore Database)

(8) Sumana Kladsomboon, Sirapat Pratontep, Theeraporn Puntheeranurak and Teerakiat Kerdcharoen, “Investigation of Thermal and Methanol-Vapor Treatments for MgTPP as an Optical Gas Sensor”, The 4th Annual IEEE International Conference on Nano/Micro Engineered and Molecular Systems (IEEE-NEMS2009), 5-8 January 2009, Sheraton Dameisha Resort, Shenzhen, CHINA. (Indexed in SCOPUS, IEEE Explore Database)

(9) Weerayut Srichaisiriwech, Anurat Wisitsoaat, Ditsayut Phokharatkul, Chanpen Karuwan, Adisorn Tuantranont and Teerakiat Kerdcharoen, “Electronic Tongue Based on Modified Carbon Nanotube Electrochemical Sensor Array”, ECTI-CON2010 - 7th International Conference of Electrical Engineering/Electronics, Computer, Telecommunications and Information Technology Association, 19-21 May 2010, Chiang Mai, THAILAND. (Indexed in SCOPUS, IEEE Explore Database)

(10) Chatchawal Wongchoosuk, Anurat Wisitsoraat, Adisorn Tuantranont, and Teerakiat Kerdcharoen, “Mobile Electronic Nose Based on Carbon Nanotube-SnO2 Gas Sensors: Feature Extraction Techniques and Its Application”, ECTI-

CON2009 - 6th International Conference of Electrical Engineering/Electronics, Computer, Telecommunications and Information Technology Association, 6-9 May 2009, Pattaya, THAILAND. (Indexed in SCOPUS, IEEE Explore Database)

(11) Piangkhwan Wanitchang, Somboon Sahasithiwat, Chakkrapan Nerungsi, Tienthong Thongpanchang and Teerakiat Kerdcharoen, "Organic light emitting devices using 9,10-bis (dodecylthio)anthracene as a new emitting material", ECTI-CON2009 - 6th International Conference of Electrical Engineering/Electronics, Computer, Telecommunications and Information Technology Association, 6-9 May 2009, Pattaya, THAILAND. (Indexed in SCOPUS, IEEE Explore Database)

PATENT

(1) ธีรเกียรติ์ เกิดเจริญ และ พนิดา หล่อวงศ์ตระกูล คำขอสิทธิบัตรหมายเลข 1101002202 เรื่อง "ชุดหัววัดไอระเหยสารประกอบแอมโมเนียและเอมีนประเภทวัสดุผสมนาโนและอุปกรณ์ตรวจวัดไอระเหยแบบมือถือ"

PROTOTYPE

(1) หัววัดไอระเหยสารประกอบแอมโมเนียและเอมีนประเภทวัสดุผสมนาโน (Amine Sensors)

(2) อุปกรณ์ตรวจวัดไอระเหยแบบมือถือ (Hand-Held Electronic Nose)

ภาคผนวก

Au-doped zinc oxide nanostructure sensors for detection and discrimination of volatile organic compounds

C. Wongchoosuk[1], S. Choopun[2], A. Tuantranont[3] and T. Kerdcharoen*[1,4]

Pure and 10% w/w Au-doped zinc oxide (ZnO) nanostructure sensors were produced and used as sensing devices in a portable electronic nose (E-nose). The nanosensors were prepared using thermal oxidation technique with sintering temperature at 700°C under oxygen atmosphere at a flow rate of 500 mL min^{-1}. The sensors were demonstrated to be sensitive to various volatile organic compounds (VOCs), especially ethanol vapour. The E-nose even with only two sensors was efficient to discriminate a number of selected VOCs. The Au-doped sensor shows a significant improvement of sensitivity. The portable E-nose can detect the difference between alcohol beverages and alcohol solutions and can distinguish the difference of white and red wines having the same percentage of alcohol.

Keywords: E-nose, Alcohol, Nanostructure, Gas sensor, Au-doped zinc oxide

Introduction

Electronic nose (E-nose) has recently become one of the most promising devices for quality control of food[1,2] and beverage,[3,4] environment protection[5] and public safety.[6] In principles, the E-nose combines an array of sensing elements with a data analysis system. Metal oxide semiconductors (MOX), such as ZnO, SnO_2 and TiO_2, are among the most popular sensing materials for E-nose. These sensors utilise the changes of electrical conductivity upon exposing to target gases. Doping these materials with some metal catalysts can enhance sensing properties. For examples, Gong *et al.*[7] reported an improvement in the sensitivity and selectivity of Cu-doped ZnO to CO. Shishiyan *et al.*[8] demonstrated that doping ZnO with Sn can increase the sensitivity of this gas sensor to NO_2. At present, most developments of selective MOX sensors are based on the ZnO thin films doped with different impurities such as Fe, Al, MnO_2, Bi, etc.[9–13] From the authors' point of view, Au is very interesting for doping in gas sensor since it is well known to be a good catalyst when they have particle size smaller than 10 nm.[14] The Au catalysts have been shown potentials for both selective and non-selective oxidation of hydrocarbons.[15–17] In addition, it was reported that Au-doped ZnO sensor exhibited and improvement of sensitivity toward ethanol.[18,19]

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In this paper, the authors have produced and examined the gas sensing properties of undoped and Au-doped ZnO nanostructure sensors. These sensors were applied in E-nose for detection of volatile organic compounds (VOCs). It was shown that the E-nose having only two sensors can discriminate various kinds of samples.

Experimental

Preparation of ZnO and Au-doped ZnO nanostructure sensors

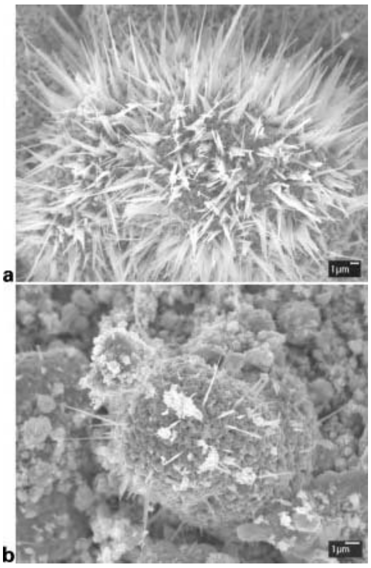
Pure and Au-doped ZnO nanostructure sensors were prepared using thermal oxidation technique. The oxidation was performed by heating zinc powder (purity 99·9%) and a mixture of zinc powder and 10 wt-%Au powder. Such mixtures were screened as a thick film onto an alumina substrate. The thick films were sintered at 700°C for 24 h under oxygen atmosphere with flow rate of 500 mL min^{-1}. The ZnO nanostructures were characterised using field emission scanning electron microscopy (FESEM). The FESEM images of ZnO and 10 wt-% of Au-doped ZnO nanostructure sensors on the alumina substrate are displayed in Fig. 1.

The wire-like or belt-like nanostructures outward from microparticle are observed. The diameter and length of ZnO nanostructures are within the range of 250–750 nm and 1·7–7·0 μm respectively. The sensors were simply fabricated by putting gold contact and heating coil underneath alumina substrate. The successfully produced ZnO and Au-doped ZnO nanostructure sensors are displayed in Fig. 2.

Portable electronic nose system

The diagram of portable E-nose system is shown in Fig. 3. It consists of three main parts:

DOI 10.1179/143307509X437572

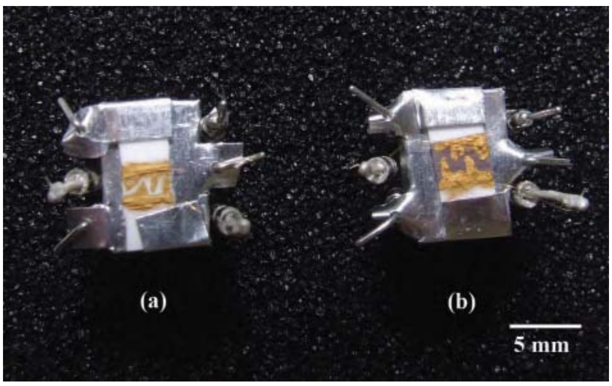


1 Image (FESEM) of *a* ZnO and *b* 10 wt-% Au-doped ZnO nanostructure

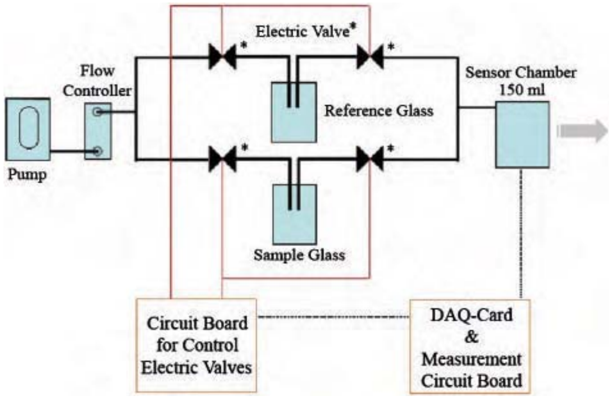
(i) sensor chamber
(ii) air flow system
(iii) DAQ card and measurement circuit.

All parts were contained in a rectangular box with a dimension of $19{\cdot}5\times29{\cdot}5\times10$ cm^3 respectively.

For the first part, the two nanostructure sensors were installed at the bottom of the chamber. The air carrying the odor molecules was introduced into the 150 mL of sensor chamber through a Teflon tube. The caliber is ~2·5 mm. The sensor chamber also has an exhaust Teflon tube which has the same caliber. The second part consists of four electrically controlled solenoid valves, sample and reference glass containers, plastic pipes and flow controller. It is necessary for this type of measurement to switch between a reference and a sample glass in order to reduce the humidity effects.[20,21] Four electrically controlled solenoid valves were used to avoid mixing of the gas from the reference and the sample. Then, the gas from the reference or sample flows to the sensor chamber of which the flow rate was set at 2 L min^{-1}. Finally, in the measurement circuit, data acquisition was realised by a USB-DAQ-Card National Instruments NI USB-6008. The measurement program was written using LabVIEW.



2 *a* ZnO and *b* 10 wt-% Au-doped ZnO nanostructure sensors used in portable electronic nose



3 Schematic diagram of dynamic portable E-nose system

Noise correction

For data analyses, DC signal of each sensor was stored every 1 s. The noise or the standard deviation (SD) of signals from ZnO and Au-doped ZnO sensors is 0·0224 and 0·0178 V. To achieve high accuracy, RMS measurements with a low side lobe window[22] were employed to apply to the signals. The main lobe is centred at each frequency component of the time domain signal and the side lobes approach zero at

$$\Delta f=\frac{F_s}{N} \tag{1}$$

where F_s is the frequency at which the acquired time domain signal was sampled. N is the number of points in the acquired time domain signal.

In the experiment, N is 1000 samples. After using mathematical correction, the SD becomes 0·0049 V for ZnO sensor and 0·0016 V for Au-doped ZnO sensors resulting in a signal to noise ratio of about 44 and 65 dB respectively.

Results and discussion

Sensor responses on VOCs

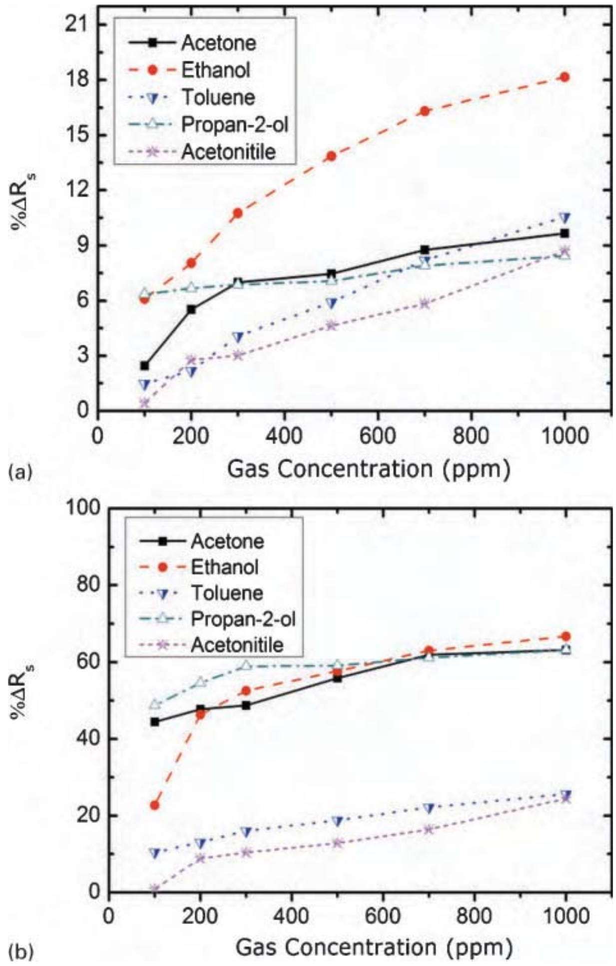
To compare sensitivity of two sensors on different VOCs, it is better to calculate the percentage change of resistance ($\%\Delta R_s$) via

$$\%\Delta R_s=\left|\frac{\overline{R}_{sam}-\overline{R}_o}{\overline{R}_0}\right|\times100 \tag{2}$$

where $\overline{R}_{sam}$ and $\overline{R}_0$ are the mean sensor resistance in the presence and absence of the testing gas respectively.

Figure 4 shows the sensor responses of pure and Au-doped ZnO to acetone, ethanol, toluene, propan-2-ol, acetonitile.

From Fig. 4, it indicates that the sensor responses of both sensors work linearly with gas concentration. At the same concentration, the sensor response of Au-doped ZnO sensor on all VOCs is higher than that of ZnO sensor. The Au in ZnO enhances the adsorption reaction between the VOCs and the adsorbed oxygen ion on the crystal surface with a negative charge. The species of oxygen ion previously determined to be O^{2-}.[23] At the grain boundaries, the surface density of the negatively charged oxygen decreases immediately and abundantly. Therefore, the changing of resistance of Au-doped ZnO sensor is much more than that of ZnO sensor. Moreover, such ZnO nanosensor shows the strong



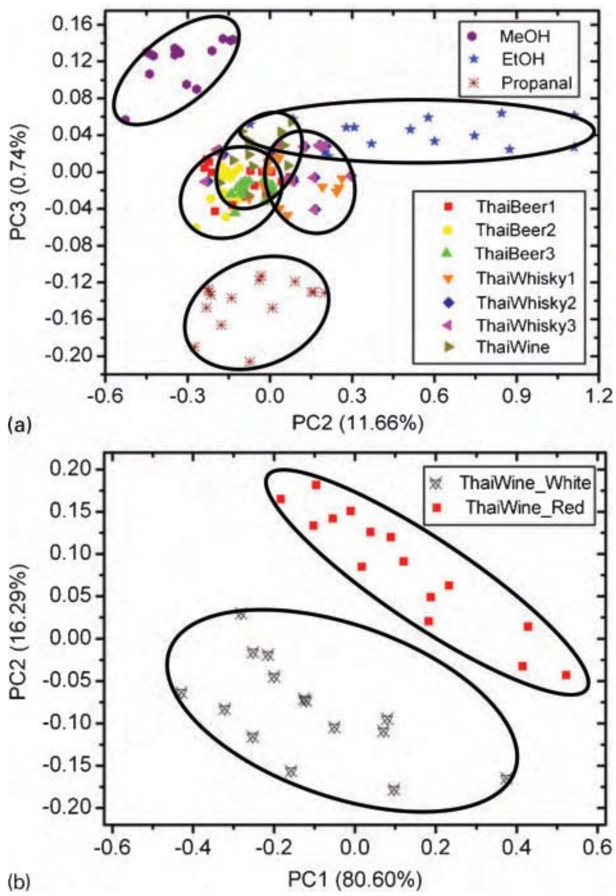
4 Sensor response of *a* ZnO and *b* 10 wt-% Au-doped ZnO sensors to concentrations of VOCs

response on ethanol. Therefore, it is suitable to employ in detecting alcoholic solution and beverages.

Detection and discrimination of alcohol samples

Because such sensors could well respond to alcohol. The ethanol, methanol, propanol and various Thai beer, Thai wine and Thai whiskey samples were measured using the E-nose based on two nanosensors. The data were introduced into the principle component analysis (PCA) for recognition and discrimination of samples. The PCA method can be used for dimensionality reduction of a dataset while retaining those characteristics of the dataset that contribute most to its variance. The input data can be the percentage change of every sensor or only some sensors for multiple measurements of different samples. However, in this E-nose, there are only two sensors. It means that the dataset only has two dimensions. Feature extraction techniques need to be applied to raw data for selecting the appropriate data and for increasing the dimension. The last 10 samples of each sensor before and after switching to another line were averaged. The difference of both values was used. Another feature can be extracted from the range of decay times. The difference of slope for the sample measurement was also used. Therefore, one experiment can give four different sensor output features.

Figure 5 shows two-dimensional PCA results for discrimination of alcohols. In Fig. 5*a*, it can be observed that the E-nose based on two nanosensors



5 Results of PCA for discriminate of *a* alcohols and *b* typical Thai wines

can discriminate quite well between the ethanol, methanol and propanol with PC2 of 11·66% and PC3 of 0·74%. Thai alcoholic beverage sample points locate around the ethanol sample points because alcoholic beverages have the contents of ethanol. However, in the case of Thai wines having the same percentage of alcohol (12·5% alcohol by volume), the E-nose can clearly discriminate the white and red wines as shown in Fig. 5*b* with PC1 of 80·60% and PC2 16·29%. The discrimination of white and red wines even with the same alcohol amount indicates that the E-nose is sensitive to other vapour ingredients apart from alcohols as well.

Conclusions

Pure and 10 wt-% Au-doped ZnO nanostructure sensors were successfully produced by using thermal oxidation technique. Doping 10 wt-%Au could improve the sensitivity of gas sensors on VOCs. The responses of the sensors are linear with gas concentrations varying from 100 to 1000 ppm. Therefore, it can be used for predicting the gas concentrations of unknown VOCs. In the real applications, only two sensors can be installed in the E-nose which is sufficiently efficient to detect and discriminate various different alcohol beverages. This E-nose can then be employed for quality control in the beverage industry. These elementary results are promising for further applications of this E-nose which can be further enhanced by using a higher number of ZnO sensors at various Au-doping percentages.

Acknowledgements

We are grateful to the Thailand Research Fund for a research career development grant (grant no. BRG5180023) given to TK, and Commission of Higher Education for a PhD scholarship given to CW. NECTEC and Mahidol University are gratefully acknowledged for supports.

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Sensors **2009**, *9*, 7234-7249; doi:10.3390/s90907234

OPEN ACCESS
sensors
ISSN 1424-8220
www.mdpi.com/journal/sensors

Article

Detection and Classification of Human Body Odor Using an Electronic Nose

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Received: 24 June 2009; in revised form: 19 August 2009 / Accepted: 3 September 2009 / Published: 9 September 2009

Abstract: An electronic nose (E-nose) has been designed and equipped with software that can detect and classify human armpit body odor. An array of metal oxide sensors was used for detecting volatile organic compounds. The measurement circuit employs a voltage divider resistor to measure the sensitivity of each sensor. This E-nose was controlled by in-house developed software through a portable USB data acquisition card with a principle component analysis (PCA) algorithm implemented for pattern recognition and classification. Because gas sensor sensitivity in the detection of armpit odor samples is affected by humidity, we propose a new method and algorithms combining hardware/software for the correction of the humidity noise. After the humidity correction, the E-nose showed the capability of detecting human body odor and distinguishing the body odors from two persons in a relative manner. The E-nose is still able to recognize people, even after application of deodorant. In conclusion, this is the first report of the application of an E-nose for armpit odor recognition.

Keywords: E-nose; body odor; biometrics; PCA; deodorant; humidity correction algorithm

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1. Introduction

Nowadays, electronic noses (E-nose) are well-known as efficient analytic devices that are widely used for many applications such as quality control of foods [1–5] and beverages [6–9], public safety [10,11], air protection [12,13] and medical applications [14–18]. Recently, there have been increasing interests in the application of E-nose for measurement of human body odors. If successful, many new applications await in such area as healthcare monitoring, biometrics and cosmetics. In principles, the human body dynamically generates unique patterns of volatile organic compounds (VOCs) under diverse living conditions such as eating, drinking, sexual activities, health or hormonal status [19]. These VOCs released from the human body can give some information about diseases, behavior, emotional state and health status of a person [20]. In addition, body odor is one of the physical characteristics of a human that can be used to identify people [21]. The human odor is released from various parts of body and exists in various forms such as exhalation, armpits, urine, stools, farts or feet. Natale *et al*. [22] developed an E-nose that can diagnose the urine odor of the patients with kidney disorders. Phillips and co-workers demonstrated the detection of lung cancer [23] and breast cancer [24] from human breath using E-nose. An E-nose was also tested to help monitor alcoholic consumption of aged persons by measuring the odors from exhalation [25]. However, to our best knowledge, no report is yet available on E-nose monitoring of human armpit odor. In fact, the armpit is a skin region where a vast number of glands and bacteria cooperate to produce a strong smell [26,27]. It can be the best source for sampling volatile chemicals released from the human body, which may give a unique pattern allowing identification of different persons.

One important obstacle to the detection the human body odor from armpits is sweat. Each day, humans produce different quantities of sweat, depending on the environment and, more importantly, life activities. Since it is well-known that most gas sensors are to some extent sensitive to humidity [28] this varying sweat content can be a problem for measurement of armpit odor samples. Therefore, a correction of the humidity effect is necessary to ensure a pure sensor response to only the volatile organic compounds that match with the identity of individual persons. Another problem for E-nose measurement of armpit odor is the disturbance from artificial chemicals such as deodorants because most adult people utilize deodorants to reduce unpleasant body odor. An interesting question arises whether E-nose can identify persons using deodorant or not? If both problems can be solved, biometrics based on armpit odor recognition would become viable.

In this paper, we propose a strategy to identify persons based on measurement of human body odor from armpits. To demonstrate this concept, we have designed and constructed an E-nose based on a set of metal oxide gas sensors. With this E-nose and the proposed method, identification of two persons either with or without using deodorant could be achieved.

2. Experimental

2.1. E-Nose System

Our lab-made electronic nose system (see Figure 1) was designed to measure VOCs generated from the human body. It is comprised of three main parts: (i) sensor chamber (ii) air flow system and (iii) data acquisition (DAQ) and measurement circuit.

Figure 1. Schematic diagram of the lab-made E-nose system.

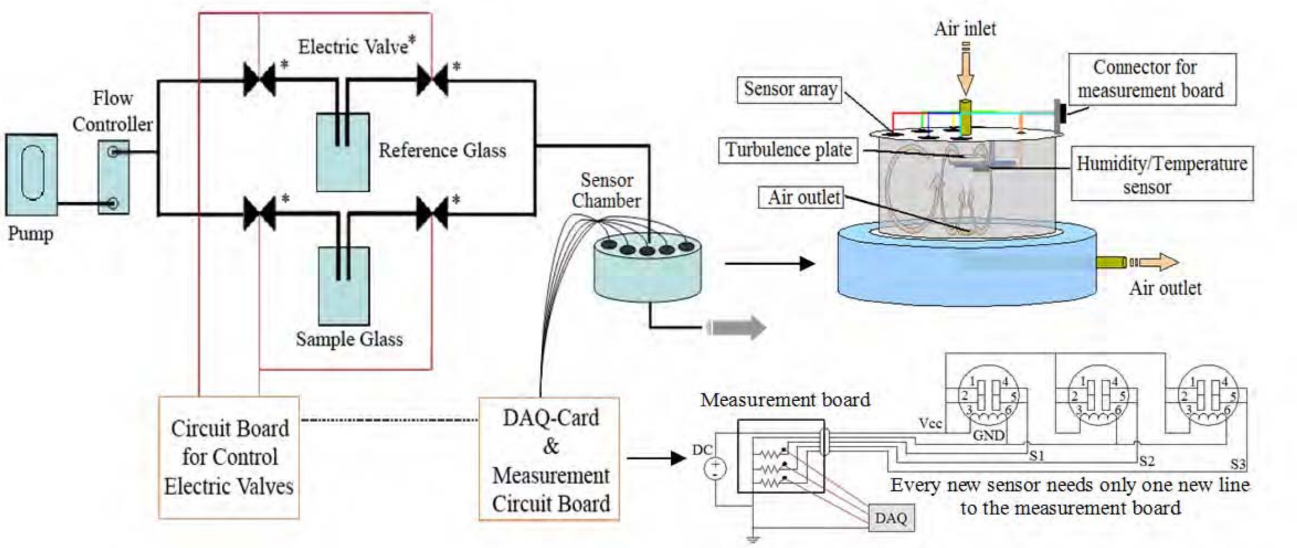

Table 1. Specifications of each metal oxide sensor.

Sensor	Target Gas	Typical Detection Ranges	Heater Power Consumption
TGS 813	Combustible gases	500–10,000 ppm	835 mW
TGS 822	Organic solvent vapors	50–5,000 ppm	660 mW
TGS 825	Hydrogen sulfide	5–100 ppm	660 mW
TGS 880	Cooking vapors	10–1,000 ppm	835 mW
TGS 2602	Air contaminants	1–30 ppm	280 mW

In this work, we have used gas sensors as commercially available from Figaro Engineering Inc. The gas sensors, as listed in Table 1, were selected in order to cover the targeted gases present in human body odor [29]. These gas sensors have been widely known as TGS (Tagushi) gas sensors since they were invented and patented by Naoyoshi Tagushi. The TGS gas sensors are usually produced by deposition of a metal oxide semiconductor (MOX), i.e., SnO_2 and WO_3, as a thin film on interdigit electrodes. Upon catalytic reactions of the metal oxide surface with the target gas molecules, usually at a temperature between 250–350 °C, the resistance between the electrodes is changed and measured. This type of gas sensors (resistive) has an advantage over other types of gas sensors (i.e., gravimetric or capacitive) that a simple circuit is required for implementation. Illustration of the circuit diagram and other details of each sensor can be obtained from the manufacturer website at http://www.figaro.co.jp/. The temperature and humidity sensor (SHT15; SENSIRION Inc.) was installed inside the sensor chamber. The sensor chamber is made of a glass cylinder sealed with Teflon plates on top and bottom. Both Teflon plates have an inlet and exhaust hole aligning oppositely. Under the inlet hole, there is a small Teflon plate to obstruct the stream of flow-in air, in order to create a turbulent that will assist in sensing by the gas sensors placed underneath the top cover. The temperature and humidity sensors are also mounted underneath this barrier plate. The air flow system