



Research Report

การสังเคราะห์อนุภาคนาโนโลหะเงินและวัสดุนาโนคอมโพสิต
สำหรับก๊าซเซนเซอร์ตรวจวัดสารระเหยเพื่อตรวจสอบคุณภาพ
ผลิตภัณฑ์ทางการเกษตร

Synthesis of Silver Nanoparticles and Nanocomposites for Volatile
Compound Gas Sensors Used in Applications of Agricultural
Quality Detection

Kriengkri Timsorn

Physics Division, Faculty of Science and Technology, Phetchabun
Rajabhat University

Budget Year 2020

Full Research Report

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ชื่องานวิจัย

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ก๊าซเซนเซอร์ตรวจวัดสารระเหยเพื่อตรวจสอบคุณภาพผลิตภัณฑ์
ทางการเกษตร

ผู้วิจัย

ดร. เกรียงไกร ทิมศร

สาขาวิชา

ฟิสิกส์

มหาวิทยาลัยราชภัฏเพชรบูรณ์ ปีเสร็จวิจัย 2563

บทคัดย่อ

งานวิจัยนี้ นำเสนอการใช้วัสดุนาโนคอมโพสิตสำหรับการผลิตก๊าซเซนเซอร์เพื่อตรวจวัดสารระเหยในการตรวจสอบคุณภาพผลิตภัณฑ์ทางการเกษตร วัสดุนาโนที่ใช้สำหรับสังเคราะห์หมึกนำไฟฟ้า ได้แก่ อนุภาคนาโนโลหะเงิน พอลิเมอร์นำไฟฟ้า และท่อคาร์บอนนาโน อนุภาคนาโนโลหะเงินถูกสังเคราะห์ด้วยวิธีที่เป็นมิตรกับสิ่งแวดล้อม (Green synthesis) โดยการใช้น้ำตาลมะพร้าวภายใต้การฉายแสงสีขาวยที่อุณหภูมิห้อง สำหรับการผลิตก๊าซเซนเซอร์นั้น หมึกนำไฟฟ้าถูกนำไปเคลือบลงบนขั้วเงินนำไฟฟ้าที่เตรียมไว้บนแผ่นพลาสติกด้วยวิธี Drop-casting หลังจากทดสอบคุณสมบัติของก๊าซเซนเซอร์ที่ผลิตขึ้นมานี้พบว่า ก๊าซเซนเซอร์ตอบสนองต่อก๊าซแอมโมเนียที่อุณหภูมิห้องได้ดีที่ระดับความเข้มข้น 300 ppm ในการวัดสารระเหยของกะหล่ำปลี ก๊าซเซนเซอร์ที่ผลิตขึ้นมาและก๊าซเซนเซอร์ชนิดออกไซด์ของโลหะ 3 ตัว ถูกนำไปวัดสารระเหย จากผลการวิเคราะห์ค่าการตอบสนองของก๊าซเซนเซอร์ต่อสารระเหยด้วยวิธี PCA และ ANN พบว่า ก๊าซเซนเซอร์ที่ผลิตขึ้นมาสามารถตรวจวัดและแยกแยะสารระเหยของกะหล่ำปลีที่เวลาการเก็บต่างๆได้อย่างมีนัยสำคัญในเชิงคุณภาพ

คำสำคัญ : ก๊าซเซนเซอร์, วัสดุนาโน, อนุภาคนาโนโลหะเงิน, คุณภาพอาหาร, สารระเหย

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ABSTRACT

Fabrication of gas sensors based on hybrid materials of conductive Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDPOOT:PSS), carbon nanotubes (CNTs) and silver nanoparticles (AgNPs) is presented. AgNPs were synthesized by green method with *Cymbopogon Citratus* leaf extract as a reducing agent under white-light illumination at room temperature. For sensor fabrication, electronic ink prepared from PEDOT:PSS, CNTs and AgNPs was deposited over interdigitated silver electrode using drop-casting. The fabricated sensor exhibited high sensing performance to ammonia at 300 ppm concentration at room temperature. For detection of volatile organic compounds (VOCs), a combination of the fabricated sensor and three metal oxide sensors including TGS2602, TGS 2620 and MQ8 was used. Based on PCA and ANN analysis, the fabricated sensor could detect and identify cabbage quality during different storage days.

Keywords : gas sensor, nanomaterials, silver nanoparticle, food quality, volatile organic compound

ACKNOWLEDGEMENTS

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Kriengkri Timsorn

August 31, 2020

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CHAPTER 1

INTRODUCTION

1.1 Background and Significance

Quality and safety of agricultural products are the primary need for consumers to ensure their health and confidence. The quality and safety of agricultural products are generally determined by their physical, chemical and microbiological characteristics in terms of smell, taste and appearance as well as contamination and adulteration. Different techniques and instruments have been developed and applied to monitoring agricultural product quality and safety during production processes, packaging, transport and storage days, such as gas-chromatography coupled to mass-spectrometry (Peris and Escuder-Gilabert. 2009), x-ray fluorescence (Fleming, Foran, Kim and Guernsey. 2015), near infrared spectroscopy (Sun, Yu, Duan and Zhu. 2014) and DNA based methods (Ganopoulos, Argiriou and Tsaftaris. 2011; Vemireddy, Archak and Nagaraju. 2007). Although these techniques and instruments show great performance for food applications but their most limitations are mainly related to complex, expensive and time-consuming processes. Moreover, well trained technicians are required to setup, handle, and make qualitative judgments. These problems cause the difficulty in monitoring food and agriculture quality and safety by general consumers at homes or markets.

In general, the human sense of smell is a simple way to detect odors released from food or beverages for first evaluating their quality and safety, but human noses get tired and dangerous with more odors or toxic gases. Gas sensors are a device that can absorb chemical molecules in gas phase and convert them into electrical signals (Mendoza, Hernández, Makarov, Febus, Weiner and Morell. 2014). Using gas sensors, such as metal

oxide semiconductor based gas sensors (MOS), for detecting chemical molecules or volatile organic compounds (VOCs) emitted by food and agriculture products has attracted attention for application in area of food and agriculture quality identification. In recent decades, different materials such as nanostructured materials, conducting polymers and hybrid materials have been intensively studied to fabricate chemical sensors used for applications in food and agriculture quality and gas detection (Timsorn and Wongchoosuk. 2019; Wongchoosuk, Subannajui, Wang, Yang, Guder, Kerdcharoen, Cimalla and Zacharias. 2014; Seekaew, Lokavee, Phokharatkul, Wisitsoraat, Kerdcharoen and Wongchoosuk 2014). Moreover, nanostructured materials such as carbon nanotubes (CNTs) and nanowires, graphene and metal nanoparticles exhibit unique properties including high surface area, high electrical conductivity and high carrier mobility etc. (Jime'nez-Cadena, Riu, and Rius. 2007; Bandaru. 2007). However, gas sensors based on a hybrid of nanostructured materials and PEDOT:PSS conductive polymer for VOCs detection in food and agriculture quality applications are less available, especially in the agricultural producing countries.

Therefore, the objective of this research is to fabricate gas sensors based on a hybrid of PEDOT:PSS conductive polymer, CNTs and AgNPs by drop-casting technique for identifying agricultural product quality during different storage days. In this research, the fabricated sensor was applied to identification of cabbage quality from VOCs detection at room temperature. Principal component analysis (PCA) and artificial neural network (ANN) were employed to analyze sensor response values.

1.2 Objectives

- 1.2.1 To synthesize AgNPs using green synthesis.
- 1.2.2 To synthesize nanocomposites by chemical and physical methods.
- 1.2.3 To fabricate gas sensors from a hybrid of PEDOT:PSS, CNTs and AgNPs.

1.2.4 To identify agricultural product quality from VOCs detection by fabricated sensor.

1.2.5 To study algorithms for VOCs classification.

1.3 Scope of Research

This research will study the performance of the fabricated sensors based on hybrid of PEDOT:PSS, CNTs and AgNPs for applications in agricultural product quality by VOCs detection. Samples used in this research were cabbage stored for six days. PCA and ANN were used to analyze sensor responses to VOCs emitted by cabbage.

CHAPTER 2

LITERATURE REVIEW

Timsorn and Wongchoosuk (2019) showed fabrication of printed room temperature gas sensors based on 2D hybrid pristine, NH_2 and N_2 functionalized multi-wall carbon nanotubes (MWCNTs)/PEDOT:PSS conductive polymer for identifying formalin contamination in squids. The sensing inks were prepared from MWCNTs dispersion in PEDOT:PSS and printed over interdigitated silver electrode on flexible and transparent substrates using inkjet printing. The fabricated sensors were exposed to different volatile organic compounds including formaldehyde, ethanol, methanol, ammonia, nitrogen dioxide and hydrogen sulfide for investigation of sensor performance. The results showed that the N_2 -MWCNTs/PEDOT:PSS

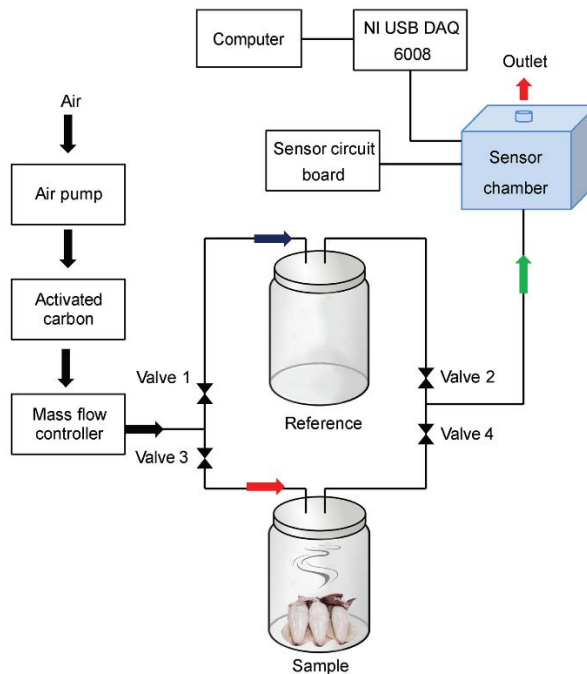


Figure 2-1 The measurement system of formalin contaminated squids (Timsorn and Wongchoosuk. 2014 : 4785).

based sensor exhibited the highest sensitivity and selectivity to formaldehyde at room temperature. Then, the fabricated sensors were applied to identification of formalin contamination in squids. The principal component analysis (PCA) provided the perfect classification between pure and formalin contaminated squids.

Seekaew, Lokavee, Phokharatkul, Wisitsoraat, Kerdcharoen and Wongchoosuk (2014) fabricated flexible printed gas sensors from graphene-PEDOT:PSS for ammonia detection. Gas sensing properties of the fabricated gas sensor were investigated by detecting various concentrations of different gases at room temperature including ammonia, diethylamine, acetone, ethanol, methanol and toluene. The result revealed that the fabricated gas sensor exhibits high response and high selectivity to ammonia in the concentration range of 25-1000 ppm. They concluded that graphene in PEDOT:PSS matrix increases effective surface area resulting in enhanced interactions between the sensing film and ammonia via π electron network.

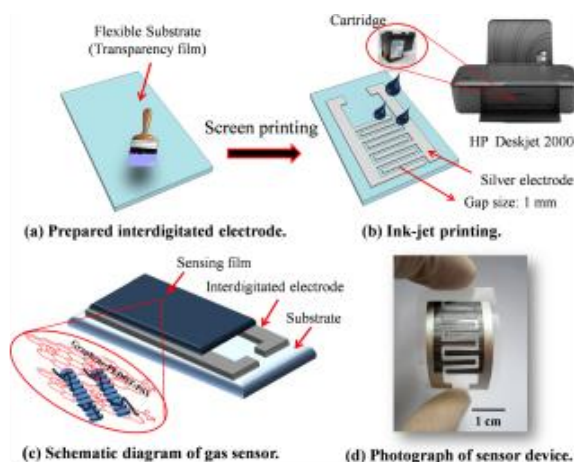


Figure 2-2 Inkjet printing of gas sensors on flexible and transparent substrate (Seekaew, Lokavee, Phokharatkul, Wisitsoraat, Kerdcharoen and Wongchoosuk. 2014 : 2974).

Pennazza, Fanali, Santonico, Dugo, Cucchiarini, Dachà, Amico, Costa, Dugo and Mondello. (2013) studied headspace evolution of white truffles during different storage conditions by using an E-nose compared with gas chromatography-mass spectrometry (GC-MS). Six Quartz Micro Balance (QMB) sensors functionalized with six different metals were used in the E-nose system. Samples were stored for seven days at 4 °C and 8 °C. E-nose and GC-MS data were studied and characterized by PCA and Least Square Discriminant Analysis (PLS-DA) was only applied to E-nose data for validation. E-nose and GC-MS results showed good agreement and found that the best storage condition was 8 °C with covering paper.

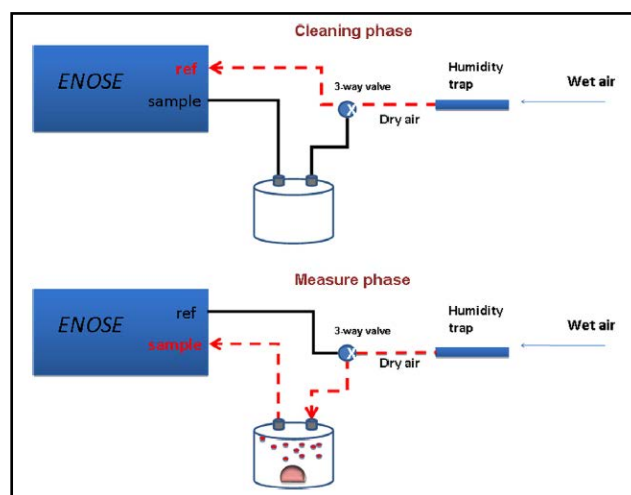


Figure 2-3 E-nose set up for white truffles measurement (Pennazza, Fanali, Santonico, Dugo, Cucchiarini, Dachà, Amico, Costa, Dugo and Mondello. 2013 : 670).

Wongchoosuk, Wisitsoraat, Tuantranont and Kerdcharoen. (2010) fabricated carbon nanotube-SnO₂ gas sensors used in an E-nose for detecting methanol (MeOH) in whiskeys. Classification techniques were integral and primary derivative. They reported that doping of carbon nanotubes (CNTs) improves the sensitivity of hybrid gas sensors. The result showed

that the E-nose based on hybrid gas sensors could monitor and classify 1 vol% of MeOH contamination in whiskeys.

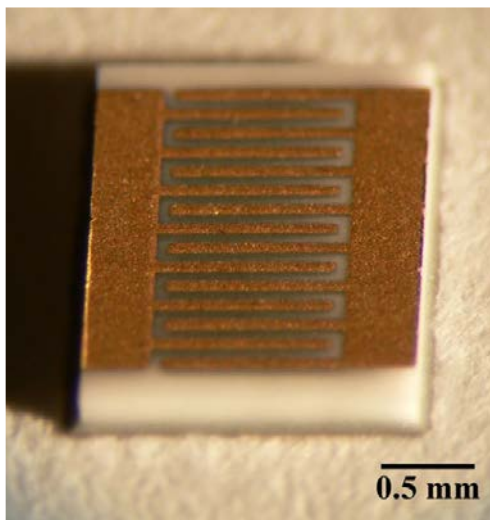


Figure 2-4 A photograph of the fabricated sensor (Wongchoosuk, Wisitsoraat, Tuantranont and Kerdcharoen. 2010 : 394).

Pranlekha, Timsorn and Wongchoosuk. (2017) synthesized silver nanoparticles (AgNPs) using green synthesis method for a low-cost flexible room-temperature humidity sensor. The *Pistia stratiotes* extract was used as a reducing agent for silver nitrate (AgNO_3) solution under light illuminations. The synthesized AgNPs were spherical shapes confirmed by transmission electron microscopy (TEM). The humidity sensor was fabricated based on AgNPs colloids with drop-coating over Ag interdigitated electrodes on transparent polyethylene substrates. The results demonstrated that the AgNPs based humidity sensor

displayed high sensitivity to relative humidity (RH) at room temperature in the RH range of 20-85%.

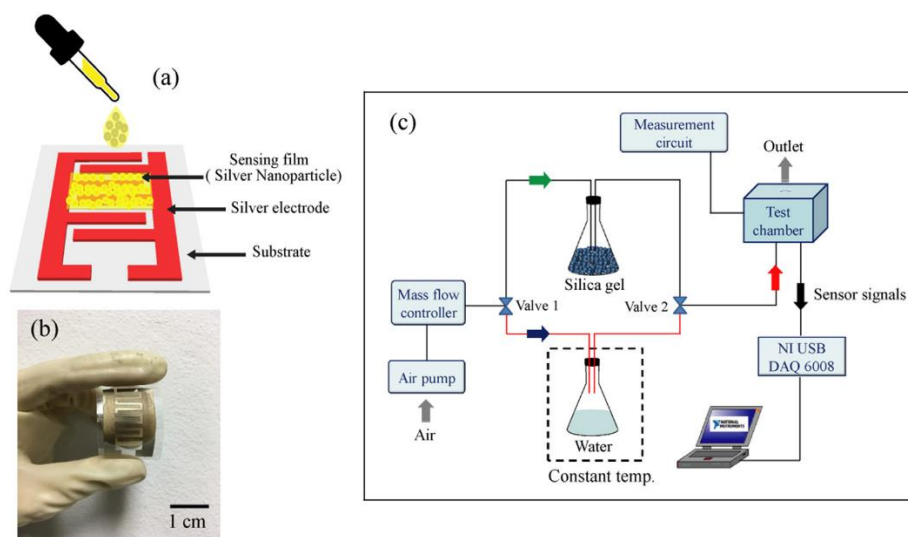


Figure 2-5 (a) Fabrication diagram and (b) a photograph of humidity sensor and (c) humidity measurement setup (Pranlekha, Timsorn and Wongchoosuk. 2017 : 3).

Manik, Nande, Raut and Dhoble. (2020) presented green synthesis of silver nanoparticles by plant leaf extraction of *Artocarpus heterophyllus* and *Azadirachta indica*. The synthesized silver nanoparticles using these plants owned average size of 20-40 nm and spherical shape. They concluded that plant leave extracts can be used as reducing agents for synthesis of silver nanoparticles without chemical reagent or template which makes this method friendly for environment.

CHAPTER 3

METHODOLOGY

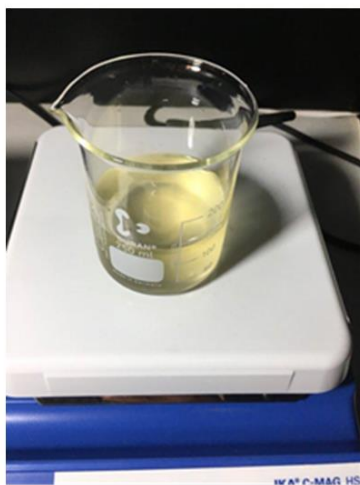
3.1 Synthesis of Silver Nanoparticles by Green Method

3.1.1 Preparation of *Cymbopogon Citratus* extract

The *Cymbopogon Citratus* was collected from Phetchabun province, Thailand. Then, fresh and healthy leaves of *Cymbopogon Citratus* were repeatedly washed with de-ionization (DI) water to clean impurities. 20 g of sliced leaves was boiled in 400 ml of DI water at 100 °C for 30 min. After boiling process, the mixtures were cooled down to room temperature and filtered using Whatman filter paper No. 4. The aqueous extract was stored at 8 °C in a refrigerator for further experiments.

3.1.2 Synthesis of AgNPs

Aqueous solution of *Cymbopogon Citratus* extract



Silver nitrate solution

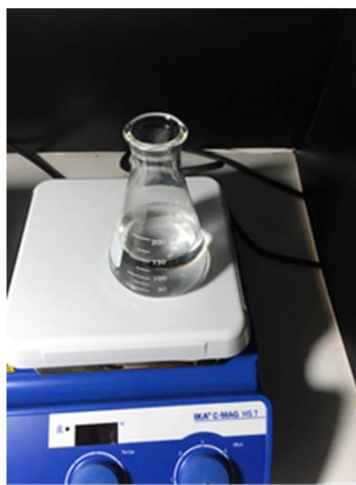


Figure 3-1 Aqueous solution of *Cymbopogon Citratus* extract and silver nitrate solution for AgNPs synthesis.

The aqueous solution of 1 and 2 mM silver nitrate was prepared by mixing silver nitrate in 400 ml of DI water. The 20 ml aqueous extract of *Cymbopogon Citratus* was added to the 20 ml of silver nitrate aqueous solution. The synthetic reaction was performed under white-light illumination emitted from a 60 W light bulb. The synthesis was carried out with pH conditions of 4 and 9 values. The pH values were adjusted by addition of hydrochloric acid (HCl) or sodium hydroxide (NaOH). The AgNPs formation could be visually observed from a change in solution color. To characterize formation of the synthesized AgNPs, Ultraviolet-visible (UV-vis) spectroscopy and transmission electron microscopy (TEM) were used. Fig 3-2 shows color changes in solution after synthesis process.

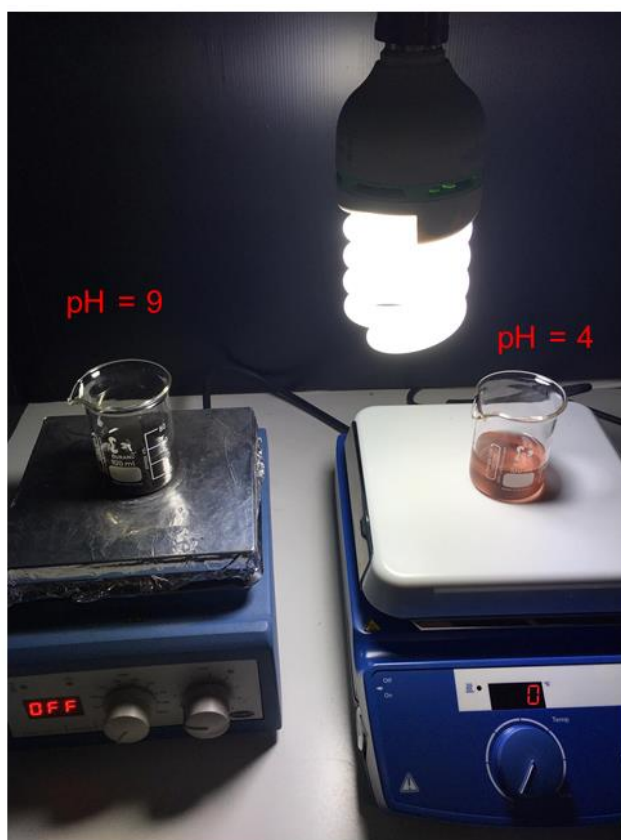


Figure 3-2 Color change in solution after synthesis process.

3.2 Nanocomposite Synthesis for Electronic Ink

The electronic ink was prepared from PEDOT:PSS, MWCNTs and AgNPs. 20 mg of MWCNTs was dispersed in 20 ml of N,N-dimethyl formamide (DMF) solution and sonicated for 20 min in order to obtain good dispersion of MWCNTs in DMF solution. After that, the suspension was filtered with Whatman filter paper No. 4 to obtain well dispersed suspension of MWCNTs. Next, PEDOT:PSS was dissolved in a mixture of 5 wt% of dimethyl sulfoxide (DMSO), 2.5 wt% of ethylene glycol (EG) and 2 wt% of triton X-100 to improve viscosity and surface tension. Then, PEDOT:PSS solution with the mixture solvent was magnetically stirred for 20 min at room temperature to obtain homogeneous PEDOT:PSS solution. For preparation of electronic ink, the well dispersed MWCNT suspension was mixed with the homogeneous PEDOT:PSS solution with a suspension to PEDOT:PSS solution volume ratio of 1:3. Then, AgNP colloid was added to a mixture of MWCNT suspension and homogeneous PEDOT:PSS solution with stirring for 45 min at room temperature. Finally, the electronic ink was obtained for sensor fabrication.

3.3 Sensor Fabrication by Drop-Casting

Firstly, interdigitated silver electrodes were prepared by depositing silver conductive paste on flexible and transparent substrates using screen printing. The rectangular electrode area was $1.5 \times 2.5 \text{ cm}^2$ with 1 mm gap size as displayed in Fig. 3-3a. The silver electrodes were dried in air at room temperature for 24 hours. The prepared electronic ink was deposited over the silver electrodes by drop-casting as showed in Fig. 3-3b and dried in air for 2 hours.

3.4 Characterization of Sensor

Surface morphology and microscopic structure of fabricated sensors were investigated by scanning electron microscopy (SEM).

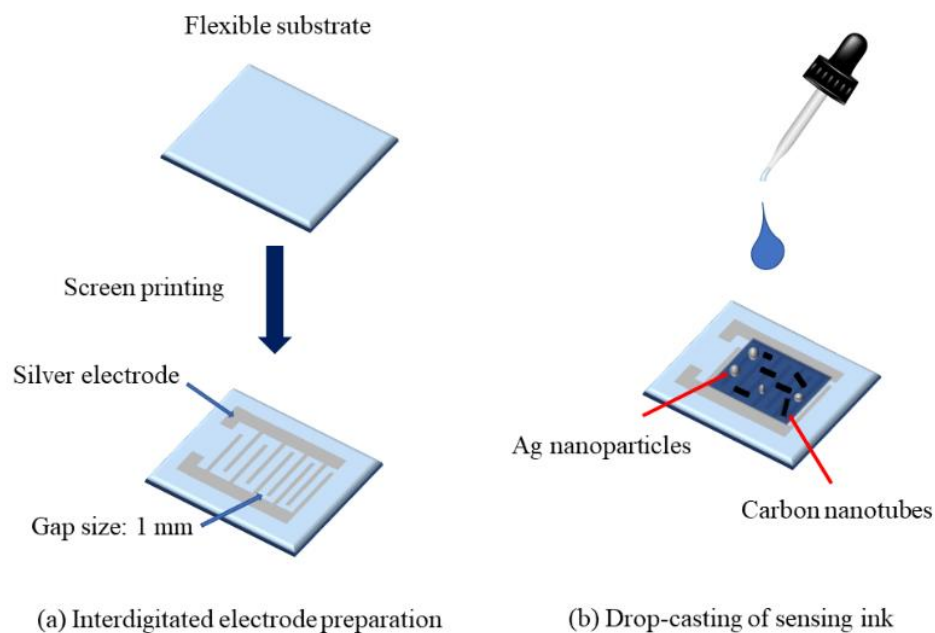


Figure 3-3 Schematic diagram of (a) interdigitated electrode preparation and (b) drop-casting of electronic ink.

3.5 Gas Sensing Measurement

To study sensor performance, the fabricated sensors were exposed toward different test gases including ammonia, ethanol and methanol. The sensors were placed in a Teflon chamber with connection of sensor circuit board at constant applied voltage (5 V). The response and selectivity of the sensors were obtained by flow-through method. The test gas sources were mixed with a constant flux of synthetic air to obtain 300 ppm of test gas concentration using mass flow controller. Each test gas was carried to the sensors in the chamber for 2 min. After gas exposure, cleaned air was delivered to clean the sensors for 2 min. All measurements were performed at room temperature (25 ± 2 °C). Changes in sensor resistances during test gas and cleaned air exposure were recorded as a function of time

using LabVIEW with NI USB DAQ 6008 used for signal collection. The sensor response can be calculated as the following equation:

$$S(\%) = \frac{(R_{\text{sens}} - R_0)}{R_0} \times 100 \quad (3-1)$$

where R_{sens} and R_0 are sensor resistance values in gas and air exposure, respectively.

3.6 VOC Measurement of Cabbage

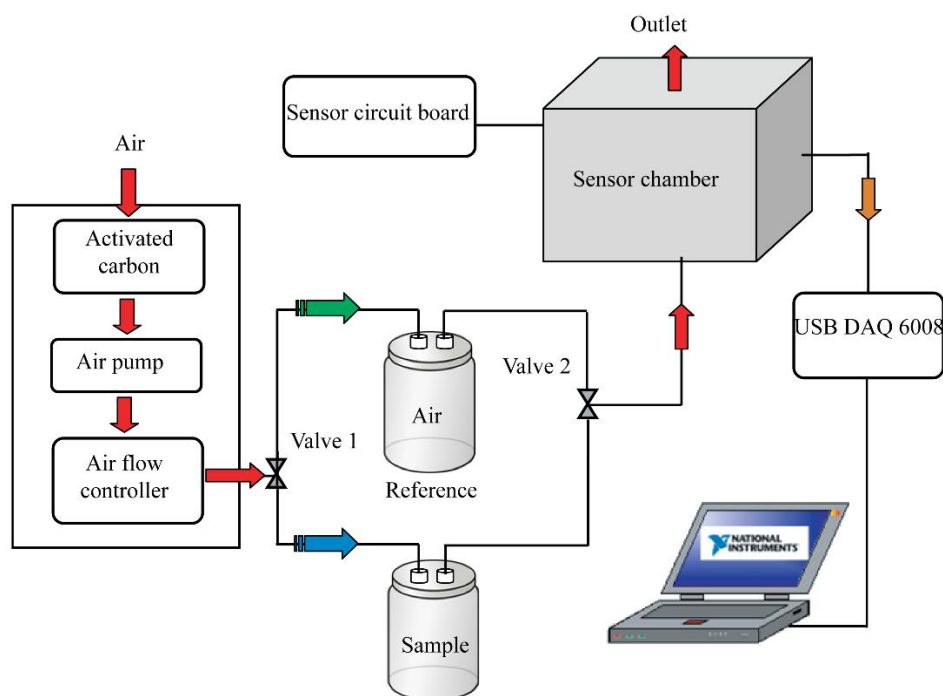


Figure 3-4 Measurement setup of VOCs emitted from cabbage.

The fabricated sensor in this work with three metal oxide gas sensors including TGS2620, TGS2602 and MQ8 was used to detect VOCs emitted by cabbage for quality identification during different storage days. Fig. 3-4 shows measurement setup used in this work. Cabbage was purchased from a local market in Phetchabun province and washed with

DI water for several time. Then, the washed cabbage was stored at 4 °C in a refrigerator for 6 days. Before measurement, the cabbage was sliced with weight of 20 g and put into a sample bottle. To start measurements, air was pumped passing an activated carbon bottle into a mass flow controller at a flow rate of 2 l/min. Clean air from the reference bottle was carried into the sensor chamber for 2 min in order to obtain baseline resistances of sensors. After 2 min, valves 1 and 2 were switched to the sample bottle. Volatile organic compounds emitted from cabbage samples were carried into the sensor chamber for 2 min. The change in sensor resistances was recorded every second as a function of time. All devices in the measurement system were controlled via our LabVIEW programming.

3.7 Data Analysis

3.7.1 Principal component analysis (PCA)

PCA is a well-known statistical method that has been widely used for data classification in various applications as well as food quality control (Timsorn and Wongchoosuk. 2019; Timsorn, Thoopboochagorn, Lertwattanasakul and Wongchoosuk. 2016; Timsorn, Lorjaroenphon and Wongchoosuk. 2017). The purpose of PCA is to reduce dimensionality of numerical data sets with retaining the most of information. It converts a data set of correlated variables into a set of uncorrelated variables using an orthogonal transformation. Each data set of uncorrelated variables is called principal components (PCs). The first principal component (PC1) contains the largest percentage of total variance. The second largest percentage is on the second principal component (PC2), and so on. The obtained new data sets are plotted and classified on two or three dimensions to visually estimate the similarities and differences between samples. The PCA result can be calculated as the following equation (Timsorn, Thoopboochagorn, Lertwattanasakul and Wongchoosuk. 2016):

$$PCA = \left(\overline{(\text{Cov}(X_{M \times N}))}_{\max @ \min} \otimes \text{Norm}(X_{M \times N}) \right)^T \quad (3-2)$$

where $\text{Cov}(X_{M \times N})$ is covariance matrix and T is transpose. M and N represent the different repetitions of measurement and a number of independent sensors, respectively. Norm is normalization of data matrix.

3.7.2 Artificial neural network (ANN)

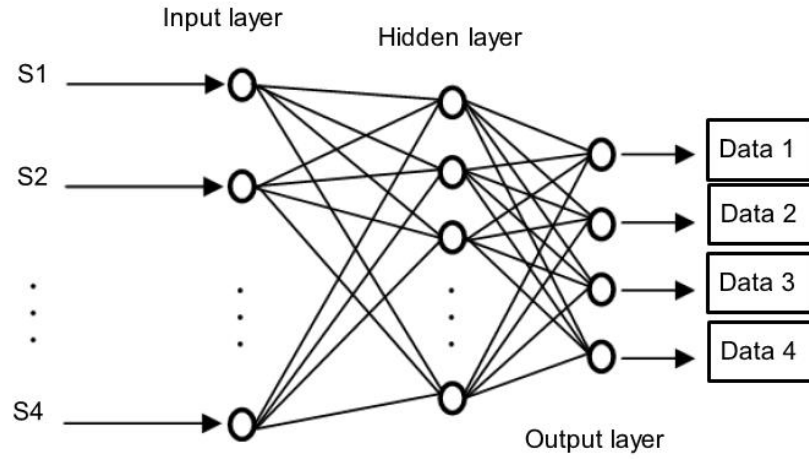


Figure 3-5 ANN network.

ANN is one of machine learning methods for learning and identifying data. Its principle mimics neural networks of human brain to transform inputs into meaningful outputs. The ANN network consists of three main layers: input layer, hidden layer and output layer. Each layer is composed of several nodes, which represent neurons in neural networks of human brain that are linked together as a network, as shown in Fig. 3-5. The input layer receives input data and contributes them towards the hidden layer. Each node in the hidden layer weights and sums its inputs corresponding to strengths of respective connection from the input layer. The outputs from nodes in the hidden layer are computed as the following equation (Balasubramanian, Panigrahi, Logue, Gu, and Marchello. 2009; Lou, and Nakai. 2001):

$$y = \sum_{i=1}^n W_i X_i \quad (3-3)$$

where y is an output of nodes in the hidden layer. X_i is input data. W_i is strengths of respective connection. Nodes in the output layer receive outputs from the hidden layer and compute them similarly. Finally, outputs of specific input data are given from nodes in the output layer. In this work, response values (S) of all sensors are input data for ANN analysis.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization of AgNPs

4.1.1 UV-vis spectroscopy analysis

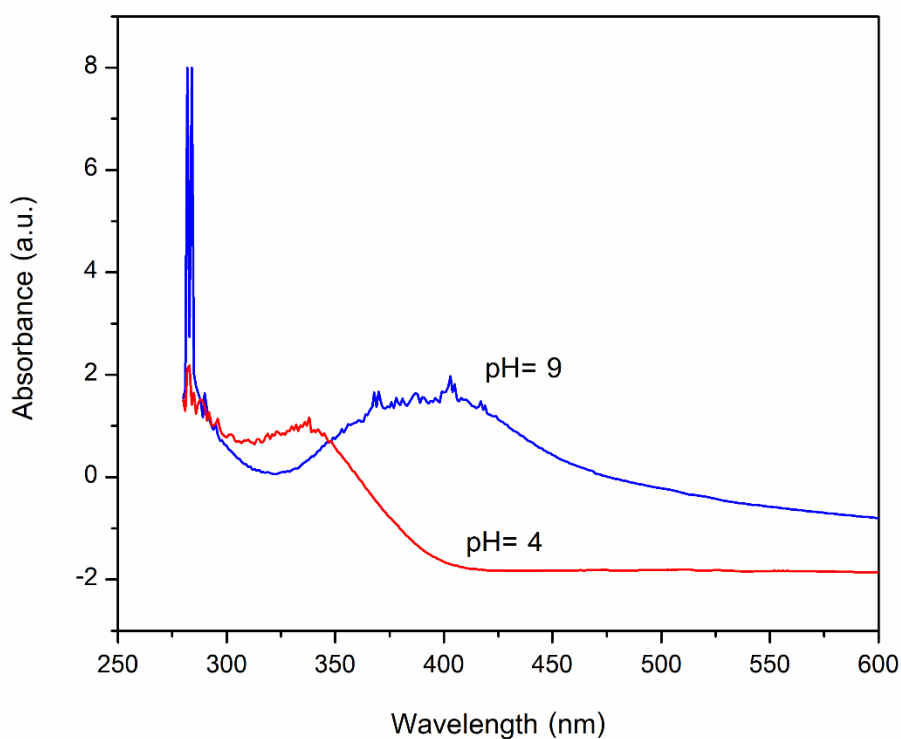
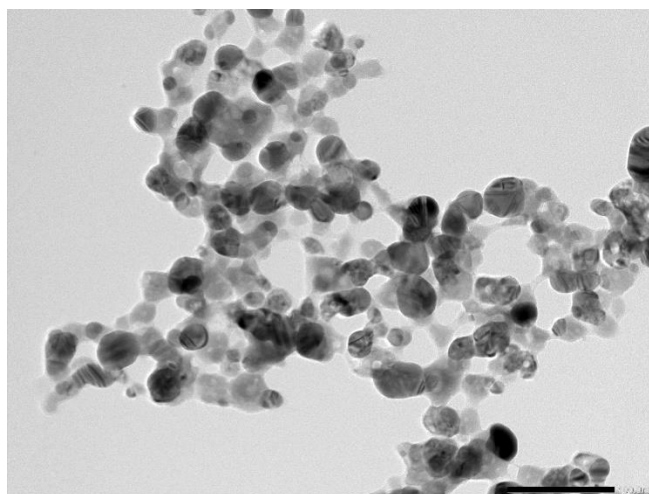


Figure 4-1 UV-vis spectra of synthesized AgNPs.

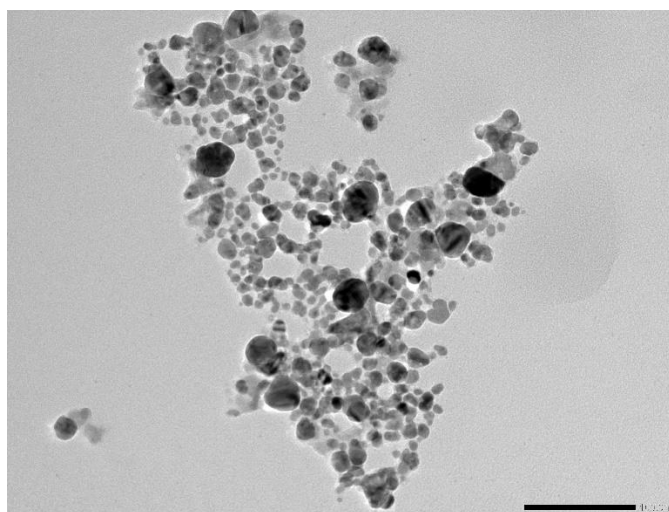
UV-vis spectra of AgNPs synthesized using AgNO_3 solution with *Cymbopogon Citratus* extract as a reducing agent under white-light illumination are presented in Fig. 4-1. It is clearly seen that the adsorption peaks of samples synthesized under influence of pH values of acidic (pH 4) and basic (pH 9) conditions appear at wavelengths of around 330 nm and 395 nm, respectively. The adsorption phenomenon of samples confirms the formation of synthesized

AgNPs from silver ions to AgNPs. The phenomenon is due to surface plasmon resonance (SPR) (Traiwatcharanon, Timsorn and Wongchoosuk. 2017).

4.1.2 TEM analysis of AgNPs



(a)

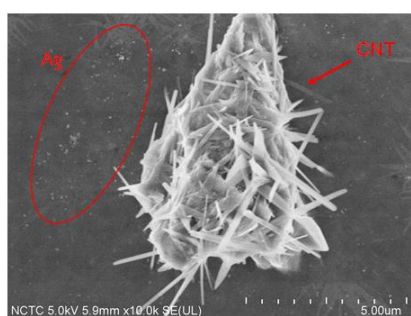


(b)

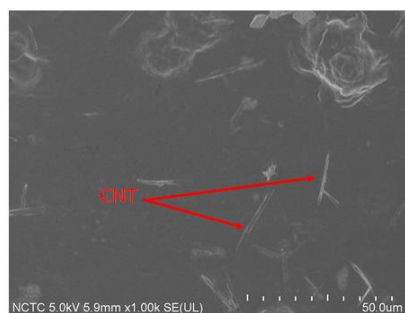
Figure 4-2 TEM images of synthesized AgNPs under influence of pH values; (a) pH 4 and (b) pH 9.

Fig. 4-2 shows TEM images of AgNPs synthesized under influence of pH values; pH 4 and pH 9. It can be seen that all samples exhibit spherical shape but the particle size depends on the pH value. The average size of synthesized AgPNs measured by ImageJ software at pH 4 (Fig. 4-2a) and pH 9 (Fig. 4-2b) was 26.74 nm and 29.76 nm, respectively. The size contributions from TEM images are well consistent with UV-vis spectra. It is clear that the AgNPs size synthesized using *Cymbopogon Citratus* extract with pH 4 of medium is smaller than AgNPs synthesized with pH 9 of medium.

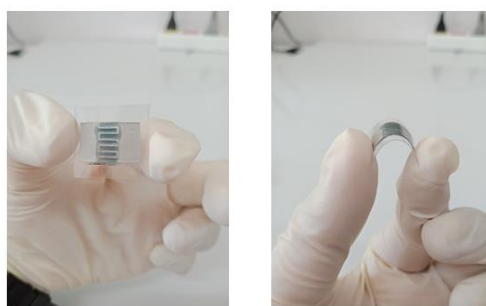
4.2 Characterization of Fabricated Sensors



(a) PEDOT:PSS/CNT/Ag



(b) PEDOT:PSS/CNT



(c) Photograph of fabricated sensors

Figure 4-3 Sem images of (a) PEDOT:PSS/CNT/AgNPs, (b) PEDOT:PSS/CNT and (c) photographs of fabricated sensors.

The surface morphology of sensors fabricated using PEDOT:PSS/CNT/AgNPs (Fig. 4-3a) and PEDOT:PSS/CNT (Fig. 4-3b) was characterized by SEM. It can be seen that CNT and AgNPs are in PEDOT:PSS matrix. This demonstrates that electronic ink prepared by PEDOT:PSS/CNT/AgNPs hybrid was successfully coated on substrates with interdigitated silver electrodes to form sensing layer of fabricated sensors. In case of PEDOT:PSS/CNT, the existence of CNT in PEDOT:PSS matrix is also observed. It should be noted that the fabricated sensor based on PEDOT:PSS/CNT is to compare with PEDOT:PSS/CNT/AgNPs for drop-casting and was not studied for gas sensing measurement. This result indicates that CNT and AgNPs in PEDOT:PSS matrix may help to increase the interactions to gas molecules.

4.3 Gas Sensing Properties

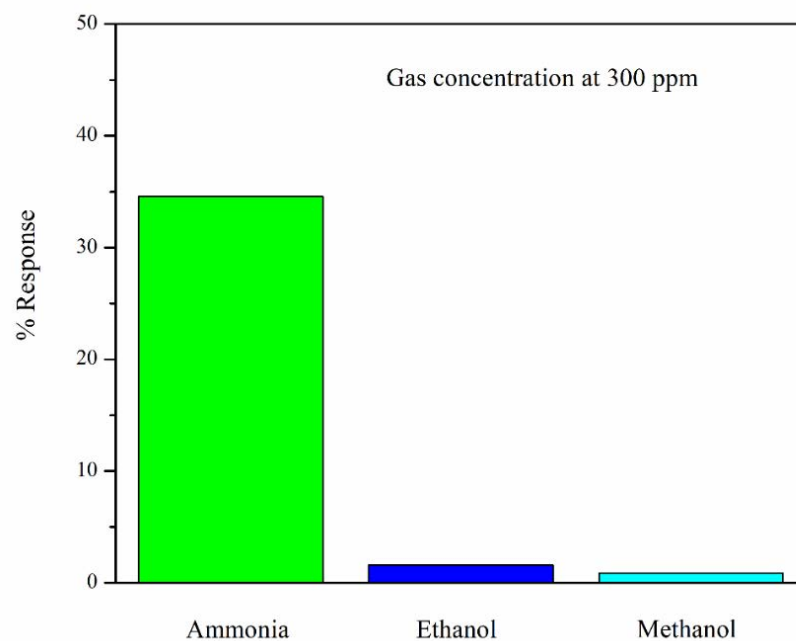


Figure 4-4 The selectivity of PEDOT:PSS/CNT/AgNPs based sensor to ammonia, ethanol and methanol at 300 ppm concentration.

To investigate the selectivity of PEDOT:PSS/CNT/AgNPs based sensor, it was exposed to 300 ppm concentration of ammonia, ethanol and methanol at room temperature. The result is showed in Fig. 4-4. It is found that the response of the sensor to ammonia, ethanol and methanol was 34.57%, 1.58% and 0.86%, respectively. From the result, the sensor exhibits the highest response to ammonia. It should be noted that ammonia is a gas mixed in VOCs emitted by agricultural products during storage days. In this work, the PEDOT:PSS/CNT/AgNPs based sensor was applied to quality detection of cabbage during storage days by detecting ammonia in VOCs.

4.4 Gas Sensing Mechanism of Fabricated Sensor

The resistance of PEDOT:PSS/CNT/AgNPs based sensor increased upon to ammonia exposure. A change in sensor resistances may be attributed to the adsorption and desorption of ammonia molecules on the sensing layer of the sensor. An increase in resistance of the sensor can be explained based on two possible mechanisms as follows (Seekaew, Lokavee, Phokharatkul, Wisitsoraat, Kerdcharoen and Wongchoosuk. 2014):

1. Reducing reaction between ammonia (NH_3) and chemisorbed oxygen (O_2^-) on the p-type PEDOT:PSS/CNT/AgNPs surface, O_2^- may be trapped at the sensor surface before NH_3 exposure. When NH_3 molecules adsorb on the surface, they react with O_2^- and provide electrons back to the surface. The reaction results in lower carrier concentrations and higher resistances of the sensor.
2. Direct charge transfer process from NH_3 to the sensor surface, when NH_3 molecules are adsorbed on the surface by physisorption, the holes of the conductive PEDOT:PSS/CNT/AgNPs receive electrons from NH_3 molecules. This process leads to lower hole concentrations and an increase in sensor resistance.

4.5 Detection of Cabbage Quality During Storage Days

4.5.1 Sensor responses to cabbage VOCs

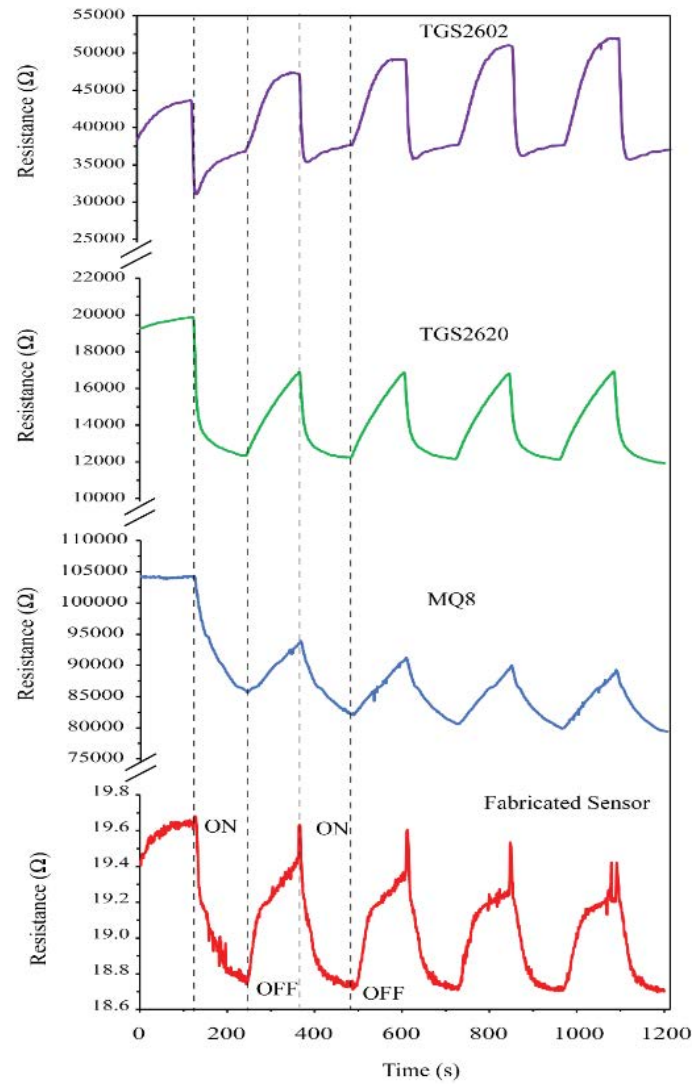


Figure 4-5 Signals of all sensors used for detection of cabbage VOCs as resistance values versus time.

Fig. 4-5 depicts signals of four sensors used for detection of cabbage VOCs during 6 storage days. One experiment was repeated five times (5 loop). It is obviously seen that the sensor resistance values of TGS2602, TGS2620 and MQ8 after sample switch (ON) quickly decreased within 10-20 s in the presence of cabbage odor. In the case of fabricated sensor (PEDOT:PSS/CNT/AgNPs based sensor), its resistance value also decreased within 20-30 s in the presence of cabbage odor. After air switch (OFF), the resistance values of all sensors returned to their baselines within 120 s. The changes in sensor resistances result from reaction between cabbage VOCs and sensing surfaces of the sensors. It should be noted that TGS2602, TGS2620 and MQ8 are n-type semiconductor based gas sensors. For the fabricated sensor, its sensing surface is based on properties of CNT, AgNPs and PEDOT:PSS.

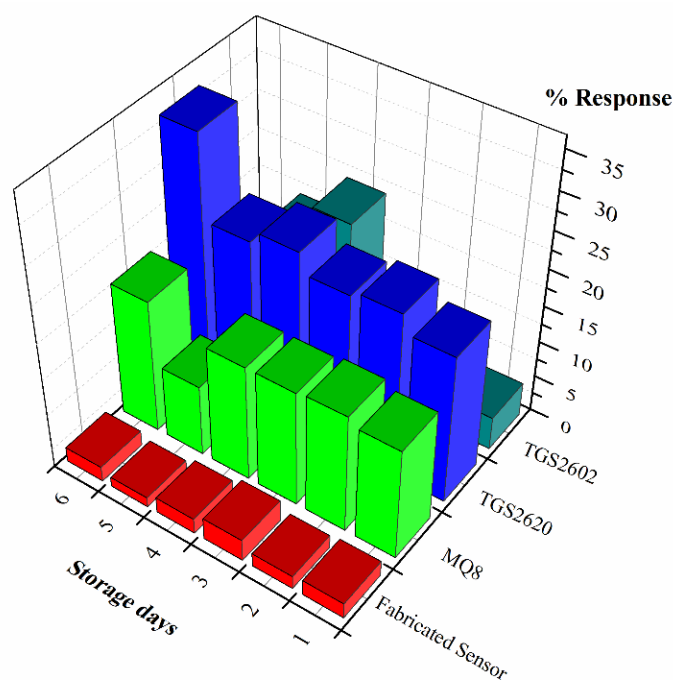


Figure 4-6 Three dimension plots of average sensor responses to VOCs emitted by cabbage during different storage days.

Fig. 4-6 shows average sensor responses to VOCs emitted by cabbage as a function of storage days. The sensor responses of TGS2602, TGS2620 and MQ8 are larger than the fabricated sensor. Trend of all average sensor responses is nonlinear with storage days. The cabbage VOCs contain both reducing and oxidizing agents which increase or decrease the amount of electrons on sensor surfaces (Timsorn, Thoopboochagorn, Lertwattanasakul and Wongchoosuk. 2016) resulting in changes in sensor responses. For the fabricated sensor, the sensor response was found to be in a range of 1.30 to 2.98%. This little response of the fabricated sensor is due to saturation of reaction between nanomaterials and VOCs emitted by cabbage.

4.5.2 PCA score plot result

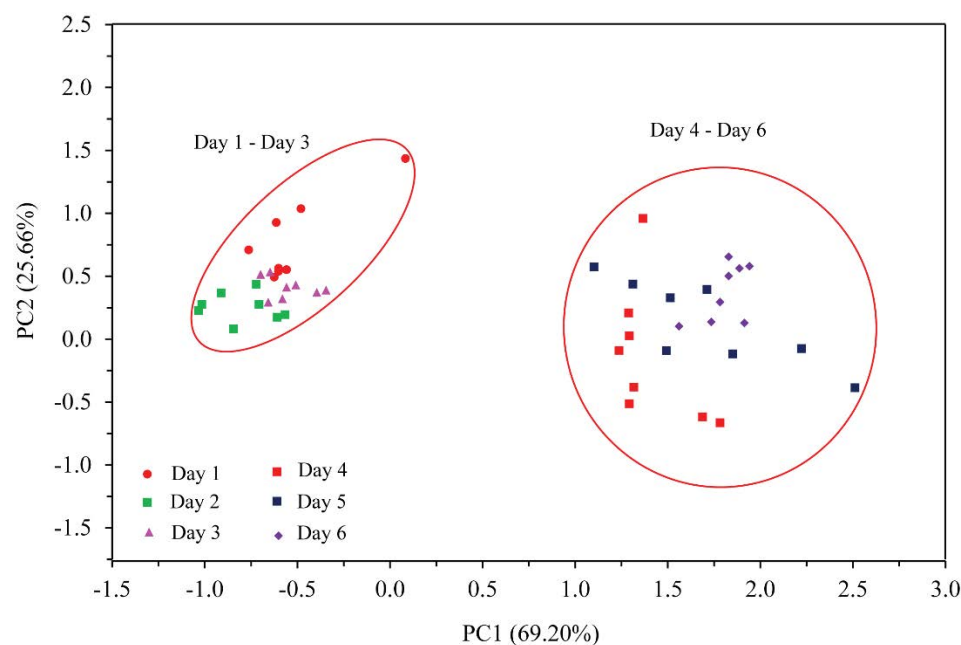


Figure 4-7 PCA score plot for classification of cabbage VOCs.

To evaluate the performance of the fabricated sensor based a hybrid of PEDOT:PSS/CNT/AgNPs for identification of cabbage quality during storage days, 240 sensor responses were introduced into the PCA. Fig. 4-7 presents PCA score plot for

discrimination of cabbage samples stored for 6 days. The PC1 explains 69.20% of the total variance and the PC2 contributes 25.66% of the total variation. The cumulative of the first two PCs represented 94.86 % of data variance which appeared to provide high enough information to explain the odor difference of cabbage samples. The PC1-PC2 plane clearly shows the separation of two main regions on PC1 axis for the samples stored for day 1- day 3 and day 4-6. These classified groups correctly correspond to only two groups of storage days. This suggests that the evolution of cabbage odors directly relates to increased storage time. During increased storage time, the VOCs in samples increase. The VOCs of day 1 – day 3 may be the same as well as day 4 – day 6 causing an overlap of PCA score in each group. It should be noted that an amount of ammonia may increase during storage days. The fabricated sensor could detect ammonia emitted by cabbage samples. Based on a combination of TGS2602, TGS2620, MQ8, the fabricated sensor and the PCA result, they confirm high performance of the fabricated sensor based PEDOT:PSS/CNT/AgNPs for identification of cabbage quality during storage days.

4.5.3 ANN result

ANN classification method was used to classify cabbage samples into different classes related to their storage days. The total number of 240 sensor responses was used as input data. The classification results are summarized in Tables 1 and 2. Table 1 presents confusion matrix of classification result for cabbage samples of each storage day. We can obviously see that the feature data are classed into 6 groups corresponding to storage days. The total correct percentage of classification is 80.00%. The correct percentages of classification of day 1, day 2, day 3, day 4, day 5 and day 6 groups are 80%, 100%, 50%, 80%, 80% and 90%, respectively. It means that the ANN analysis shows better classification than the PCA based on the same sensor responses. For result comparison with the PCA, the sensor responses were classified into two groups corresponding to day 1 – day 3 and day 4 – day 6 of storage days and introduced as input data for ANN analysis. Table 2 shows confusion

matrix of classification result corresponding to two groups (day 1 - day 3 and day 4 - day 6) of cabbage storage days. The correct percentages of each group equally reach to 96.67%. This ANN result shows good agreement with the PCA.

Table 1 Confusion matrix of classification result obtained from ANN method for different cabbage storage days.

Storage Days	Classification Results (80.00%)						Correct Percentage (%)
	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	
Day 1	8	0	1	1	0	0	80.00
Day 2	0	10	0	0	0	0	100.00
Day 3	3	1	5	0	0	1	50.00
Day 4	1	0	1	8	0	0	80.00
Day 5	0	0	0	0	8	2	80.00
Day 6	0	0	0	0	1	9	90.00

Table 2 Confusion matrix of classification result corresponding to two groups (day 1 - day 3 and day 4 - day 6) of cabbage storage days.

Storage Days	Classification Results (96.67%)		Correct Percentage (%)
	Day 1- Day 3	Day 4- Day 6	
Day 1- Day 3	29	1	96.67
Day 4- Day 6	1	29	96.67

CHAPTER 5

CONCLUSION

For this research, we are motivated to study and fabricate gas sensors using a hybrid of PEDOT:PSS, CNT and AgNPs for applications in cabbage quality identification. AgNPs were synthesized by green method. *Cymbopogon Citratus* leaf extracts were used as a reducing agent for AgNO_3 under white-light illumination at room temperature. For sensor fabrication, PEDOT:PSS, CNT and synthesized AgNPs were employed to prepare electronic ink. The prepared electronic ink was coated over interdigitated silver electrodes on flexible and transparent substrates with drop-casting. Then, the fabricated sensor and three metal oxide semiconductor sensors including TGS2602, TGS2620 and MQ8 were applied to detection of VOCs emitted by cabbage during different storage days. In the part of data analysis, PCA and ANN were used to analyze sensor data (sensor responses) and provide qualitative information of odors in the pattern of odor classification, identification and evaluation. The conclusion of research results can be summarized as follows:

1. From TEM analysis, the synthesized AgNPs exhibit spherical shape with average size of 26.74 nm and 29.76 nm for pH 4 and pH 9 of mediums, respectively. The synthesis reaction is $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}^0$. UV-vis spectroscopy confirms information of AgNPs with adsorption peaks due to surface plasmon resonance.
2. A sensor based a hybrid of PEDOT:PSS, CNT and AgNPs was successfully fabricated by drop-casting. It shows high sensing performance to NH_3 with 300 ppm concentration at room temperature. The high response of the fabricated sensor to NH_3 is due possibly to the increase of specific surface area. In case of detection of VOCs emitted by cabbage, the sensor exhibits fast response to VOCs of cabbage within 20-30 s. Its resistance decreases in the presence of cabbage VOCs. This indicates higher concentration of charge carrier on the sensor surface.

The sensor responses of the fabricated sensor to cabbage VOCs are in a range of 1.30 to 2.98%.

3. Based on PCA and ANN analysis, PCA could classify sensor responses into two groups; day 1- day 3 and day 4 – day 6 of storage days. ANN shows better classification than PCA. It is found that the total correct percentages of classification by ANN are 80.00% and 96.67% for each storage day and two groups of storage days, respectively. The obtained results from PCA and ANN can be used to interpret identification, classification and evaluation of cabbage quality during different storage days.

According to these results, it can be concluded that the fabricated sensor based a hybrid of PEDOT:PSS, CNT and AgNPs has high potential for detection of agricultural quality.

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CURRICULUM VITAE

1. Name – Surname Dr. Kriengkri Timsorn
2. Position Lecturer
3. Address Physics Division, Faculty of Science and Technology,
Phetchabun Rajabhat University, Muang District, Phetchabun
67000, Thailand
4. Education Ph.D. in Physics, Kasetsart University, Bangkok, Thailand
M.S. in Physics, Kasetsart University, Bangkok, Thailand
B.S. in Physics, Kasetsart University, Bangkok, Thailand
5. Academic Field of Specialty Electronic senses, i.e. electronic nose etc.
Gas sensors
Nanostructure materials, hybrid materials and graphene etc.
Smart instruments and systems
SCC-DFTB calculation
6. Publications 1. K. Timsorn, and C. Wongchoosuk. 2020. “Adsorption of
NO₂ HCN, HCHO and CO on pristine and amine
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charge density functional tight-binding method”, *Materials
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7. Awards

รางวัลผลงานประดิษฐ์คิดค้น ประจำปี ๒๕๖๑ รางวัลประกาศ
เกียรติคุณ เรื่อง ปันตรวจวัดการปนเปื้อนสารฟอร์มาลีนในอาหาร
แบบพกพาได้ จากสำนักงานคณะกรรมการวิจัยแห่งชาติ (วช)