INTERDIGITATED ELECTRODE (IDE) SENSOR OF POLYANILINE (PANI) NANOPARTICLES THIN FILM FOR DETECTION OF METHANOL VAPOUR

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UNIVERSITI MALAYSIA PERLIS
2012

INTERDIGITATED ELECTRODE (IDE) SENSOR OF POLYANILINE (PANI) NANOPARTICLES THIN FILM FOR DETECTION OF METHANOL VAPOUR

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A thesis submitted
in fulfillment of the requirements for the degree of
Master of Science (Material Engineering)

School of Materials Engineering
UNIVERSITI MALAYSIA PERLIS

2012

APPROVAL AND DECLARATION SHEET

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ACKNOWLEDGEMENTS

In the name of Allah The Most Gracious and The Most Merciful.

Thank to Allah for his love, blessings and enlightenment that allowed for the successful completion of this thesis as part of my Master of Science (Material Engineering) at University Malaysia Perlis. I wish to express sincere gratitude to my supervisor, Prof Dr. Mohd Noor Ahmad through whom that I have learned a lot and for his unfailing patience and guidance with regards to this master research. I am also extremely thankful my co-supervisor Dr. Supri Abd Ghani for giving a lot of advice and encouragements for my academic and research efforts.

It would have been impossible for me to complete my master without the help from sensor technology and application group member and lecturers from School of material especially Prof Dr. Ali yeon Md Syakaff, En Ammar Zakaria, Abu Hassan, Abd Hallis, Dr Irwana and En. Tulus Ikhsan who have continuously aided in the successful completion of this Research.

I thank my fellow colleagues of seniors and juniors at the sensor technology and application group and at the School of Materials Engineering for sharing their time, expertise and humour with me. They are particularly Pak Iqmal, Fathi, Seskya, Mohd Nasha 'Ain, Faroq and Azharudin.

Lastly, a very big thank you to my beloved family for their support, love and constant encouragement the have bestowed upon me. Without their support, I would never have gotten so far.

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LIST OF ABBREVIATIONS

Al	aluminum
APS	ammonium persulfate
B	benzenoid
CERHR	center for the evaluation of risks to human reproduction
CHEMFET	chemically sensitized field effect transistor
CP	conducting polymer
CV	coefficient of variability
C=C	carbon double bond
DAQ	data acquisition
DBSA	dodecylbenzenesulfonic acid
EB	emeraldine base
ES	emeraldine salt
FTIR	fourier transform infrared spectroscopy
HCl	hydrochloric acid
HCSA	camphorsulfonic acid
IDE	interdigitated electrode
LB	leucoemeraldine
LB	langmuir-blodgett
LbL	layer-by-layer
N	nitrogen-containing
NanoPANI	polyaniline nanoparticles
NH_4^+	ammonium
OM	optical microscopy
PA	polyacetylene
PANI	polyaniline
PANI-ES	polyaniline – emeraldine salt
PB	pernigraniline
Pd/PANI	palladium/polyaniline
PEDOT	poly (3,4-ethylene-dioxythiophene)

PEDOT/PSS	poly (3, 4-ethylenedioxythiophene)/poly (styrenesulfonate)
PET	polyethylene terephtalate
PPE	poly (phenylene ethynylene)
PPV	poly (phenyl vinlene)
PPY	polypyrrole
PTH	polythiophene
PVC	polyvinyl chloride
Q	quinoid
QCM	quartz crystal microbalance
RMS	root mean square
SAW	surface acoustic wave
SDS	sodium dodecyl sulfate
SEM	scanning electron microscopy
SO_3^-	sulphite ion
VOC	volatile organic compound

LIST OF SYMBOLS

A^-	charge balancing counter-ions
ppm	parts per million
rpm	revolutions per minute
S1	7 prints
S2	14 prints
S3	21 prints
S4	28 prints
V1	valve 1
V2	valve 2
V3	valve 3
V4	valve 4
v/v	volume per volume
cP	centipoise
dy/cm	dyne per centimetre

SENSOR INTERDIGIT (IDE) DARI FILEM NIPIS NANOPARTIKEL POLIANILINA (PANI) UNTUK PENGESANAN WAP METANOL

ABSTRAK

Metanol dilepaskan ke persekitaran melalui penggunaan industri atau secara semulajadi daripada gunung berapi, tumbuh-tumbuhan dan mikrob. Pendedahannya boleh berlaku dari udara persekitaran dan semasa penggunaan pelarut. Ia mempunyai ketoksikan yang tinggi kepada manusia. Jika terminum, sebagai contohnya 10ml metanol tulen boleh menyebabkan kebutaan kekal dan 30ml boleh membawa maut. Tesis ini melaporkan satu kajian pada sensor interdigit (IDE) dari filem nipis nanopartikel PANI untuk pengesanan wap methanol. Penyelidikan ini meliputi pembangunan sensor, kaedah pencirian nanopartikel PANI dan rekabentuk satu sistem pengesanan IDE. IDE telah difabrikasikan menggunakan teknik penyejatan pada substrat polietilena tereftalat (PET) dengan aluminum dijadikan sebagai elektrod. Lebar dan jurang sensor ini adalah 0.25 mm dan 0.51 mm. Nanopartikel PANI telah disintesis menggunakan kaedah pempolimeran emulsi. Kaedah semburan dakwat bercetak telah digunakan untuk menambahkan nanopartikel PANI pada IDE. Didapati saiz nanopartikel PANI adalah 152 nm. Analisis FTIR spektrum memperlihatkan kehadiran garam emeraldin polianilina (PANI-ES) dengan kewujudan puncak-puncak pada 3321, 1637, 1204 dan 1037 cm^{-1}. UV-Vis spektrum bagi nanopartikel pANI menunjukkan kehadiran tiga peralihan jalur pada 340, 420 dan 790-800 nm. Kerintangan semburan dakwat bercetak bagi lapisan nanopartikel PANI ke atas bilangan cetakan menunjukkan penurunan dari 8.34 kepada 3.24 MΩ. Permukaan semburan dakwat bercetak lapisan nanopartikel PANI akan menjadi lebih licin dan seragam dengan peningkatan jumlah cetak dan kehomogenan yang baik dapat diperhatikan pada cetakan ke 21 dan 28. Morfologi lapisan berliang dengan taburan liang tidak seragam telah dilihat melalui SEM. Didapati saiz taburan liang menjadi semakin besar selepas pendedahan kepada wap metanol menunjukkan berlakunya resapan gas. Peningkatan bilangan cetakan menunjukkan masa tindak balas meningkat dan keluaran voltan menurun tetapi masa pemulihan tidak berubah. Tujuh cetakan menunjukkan sensor yang optimum dengan masa tidak balas adalah 10s. Kebolehulangan dan kebolehasilan yang baik dapat dilihat dengan hasil respons yang tetap. Analisis kepekaan menunjukkan pengurangan kepekatan wap metahol akan mengurangkan keluaran voltan. Had pengesanan sensor ini adalah 20 ppm. Analisis pemilihan menunjukkan peningkatan rangkaian karbon bagi alkohol akan mengurangkan keluaran voltan. Jangka hayat simpanan bagi sensor ini adalah 28 hari.

INTERDIGITATED ELECTRODE (IDE) SENSOR OF POLYANILINE (PANI) NANOPARTICLES THIN FILM FOR DETECTION OF METHANOL VAPOUR

ABSTRACT

Methanol is released to the environment during industrial uses or naturally from volcanic gases, vegetation, and microbes. Exposure may occur from ambient air and during the use of solvents. Methanol has a high toxicity to humans. If ingested, for example, as little as 10 ml of pure methanol can cause permanent blindness, and 30 ml is potentially fatal. This thesis reports a study on interdigitated electrode (IDE) sensor of PANI nanoparticles thin film for detection of methanol vapour. The research covers the sensor development, characterization method of PANI nanoparticles and setting up a IDE detection system. IDE was fabricated by evaporation technique on polyethylene terephthalathe (PET) substrate using aluminum as electrode material. The digit width and gap of the sensor were 0.25 mm and 0.51 mm. PANI nanoparticles was synthesized by emulsion polymerization method. Inkjet printing method was used to deposit the PANI nanoparticles onto IDE. The size of PANI nanoparticles was 152 nm. FTIR spectra analysis correspond to well-doped PANI-ES with the existence of peaks at 3321, 1637, 1204 and 1037 cm^{-1}. UV-Vis spectra of the PANI nanoparticles shown the three band transitions appear at 340, 420 and 790-800 nm. Resistance of inkjet-printed PANI nanoparticles films was decreased over number of prints from 8.34 to 3.24 MΩ. The surface of the inkjet-printed PANI nanoparticles films became smoother and more uniform with increasing number of prints and good homogeneity could be observed at 21 and 28 prints. Porous film morphology with non-uniform pores distribution was observed by SEM. The size of pores distribution to be bigger after exposure to methanol vapour indicated that diffusion gas molecule had occurred. Increasing the number of prints shown that the response time increase and output voltage was decreased but recovery time not changing. Seven print shown the optimum sensor with response time 10s. Good repeatability and reproducibility was observed by constant response. Sensitivity analysis shown that decreasing the concentration of methanol vapour would decrease the output voltage. The limit detection of the sensor was 20 ppm. Selectivity analysis express that an increasing the carbon chain of alcohols will be decrease the output voltage. The shelf life of this sensor was 28 days.

CHAPTER 1

INTRODUCTION

1.1 Introduction

The exposed of volatile organic compounds (VOC) in human life is worrying because it may adversely affect human health. As we know that, VOC are emitted from certain solids or liquids. VOC include a variety of chemicals, some of which may have short and long term adverse health effects such as eye, nose, throat irritation, headaches, loss of coordination, nausea, damage to liver, and kidney (Kampa & Castanas, 2008). These organic compounds tend to release by a wide array of products such as cleaning supplies, pesticides, building materials and furnishings, office equipment, craft materials, photographic solutions and household products like paints, varnishes and wax. Fuels also are made up of organic chemicals. All of these products can release organic compounds while using them, and to some degree, when they are stored.

Alcohols are a class of organic compounds formed from hydrocarbons by the substitution of one or more hydroxyl groups for an equal number of hydrogen atoms. Some common alcohols are methanol, ethanol, 2-propanol (isopropyl alcohol), phenol and ethylene glycol. Ethanol is commonly known because it has countless applications as a solvent for organic chemical. Besides, this alcohol is the only least toxic of the straight-chain alcohols and our bodies can metabolize by produce an enzyme (Chang, 2005). The most dangerous alcohol is methanol because it is highly toxic and ingestion of only a few milliliters can cause nausea and blindness. In June 1998, methanol was identified for evaluation by the Center for the Evaluation of Risks to Human Reproduction (CERHR) based on high production volume, extent of human exposure, and published evidence of reproductive or developmental toxicity (Shelby et al., 2004). The effect of methanol to human life can be exposed through environmental sources such as air, water and contact with methanol containing consumer products.

Due to the high levels of toxicity and adverse effects in humans, then a detection and analysis system should be developed to detect methanol vapour. Gas sensor is an effective tool to detect toxic substances and has a great potential for developed. A gas sensor can be described as a device, which upon exposure to a gaseous chemical compounds, alters one or more of its physical or chemical properties in a way that can be measured and quantified directly or indirectly (Joshi & Singh, 2010). Actually gas sensors, chemosensors, chemical gas sensors, or biosensors can be classified according to their operating principle and each class having different characteristics. Gas sensors usually utilize an electrical or optical response by adsorption of gas molecules on surface of an active sensing layer. This makes them commonly used for industrial, commercial and residential applications.

Conducting polymer (CP)-based gas sensors have received considerable interest in recent years because of their sensing ability, high sensitivities, short response times, easily synthesized and operate at room temperature (Bai et al., 2007). Trojanowicz (2003) described CP as polymers with spatially extended π-bonding systems obtained by electrochemical polymerization or chemical oxidation of their monomer. The common feature of CP materials is the presence of a conjugated π-electron system which extends over the whole polymer. Wilson & Baietto (2009) said that CP gas sensors operate based on changes in electrical resistance caused by chemical reaction or adsorption of gases onto the sensor surface. It consist of a substrate, such as silicon, glossy paper (Arenaa et al., 2010) or polyethylene terephthalate (PET) (Cattanach et al., 2006), a pair of gold-plated electrodes (interdigitated electrode, IDE) and a conducting organic polymer coating as the active sensing layer (Schaller et al., 1998).

There are several CP used as the active sensing layers of gas sensor such as Polyacetylene (PA), Polyaniline (PANI), Polypyrrole (PPY), Polythiophene (PTH), Poly(3,4-ethylene-dioxythiophene) (PEDOT) and Poly(phenyl vinlene) (PPV) (Bai & Shi, 2007). PANI is most common used in gas sensor because of its good stability and outstanding properties compared to other CP (Bhadra et al., 2009). It is one of the so-called doped polymers, in which conductivity results from a process of partial oxidation or reduction. Bhadra et al. (2009) has provided different methods for the synthesis of PANI such as chemical, electrochemical, template, enzymatic, plasma and photo. Basically, chemical polymerization is divided into heterophase, solution, interfacial, seeding, metathesis, self-assembling, and sonochemical polymerizations. In this research, heterophase polymerization has been used to synthesis PANI into nanoparticles. This polymerization as called nanodispersion method.

In deposition of PANI films, different methods exist to deposit PANI onto a substrate including electrochemical deposition, dip-coating, drop-coating, spin coating, and Langmuir-Blodgett (LB) (Nicolas-Debarnot & Poncin-Epaillard, 2003). However, these methods present a number of limitations such as thickness control and industrial productivity. Inkjet printing is very interesting method to deposit PANI because it familiar as a method for printing on paper (Mabrook et al., 2006a). The advantages of this method compared to other methods are that it is non-contact, high speed, and can form very thin films or build thick layers (Calvert et al., 2004). Mabrook et al. (2006a) used a commercial HP thermal printer to print polypyrrole film for alcohol vapour detection at room temperature. They found that the conductivity was increased when the films is exposed to the vapours of simple alcohols.

1.2 Problem Statements

Conducting polymers (CP) are an attractive subject of research because of the interesting properties and many application possibilities. Among the available CP, PANI is found to be the most promising because of its ease of synthesis, low cost monomer, tunable properties, and good stability compared to other CP. However, the main problem associated with the effective utilization of all CP including PANI is inherent in their lower level of conductivity, their infusibility, hygroscopic and poor solubility in all available solvents (Rao et al., 2003; Cho et al., 2005).

According to Bhadra et al., (2006; 2008), the solubility and processability of some CP can be improved through doping with a suitable dopant or modifying the starting monomer. However, the selection of dopant should be based on synthesis methods, films deposition and applications to be used. Besides that, by using the inkjet printer, PANI should conform to quality printer ink in terms of viscosity and surface tension so that the ink does not drop out from the printer heads. Likewise, particles size of PANI should be smaller than the size of the nozzle printer heads to prevent the nozzle from clogging.

Therefore, studies in the synthesis of PANI with nanodimentional control have been managed to overcome this issues.

1.3 Objective of Studies

The objectives of research are:

i. To investigate the physical properties of inkjet-printed thin film PANI nanoparticles.
ii. To investigate the effect of number of printed layers (film thickness) on the sensing performance of the sensor.
iii. To investigate sensing properties of the inkjet-printed PANI nanoparticles thin film towards methanol vapour using IDE gas sensor.

1.4 Scope of Works

This research was focused on the study of interdigitated electrode (IDE) sensor of PANI nanoparticles thin film for detection of methanol vapour. Firstly, an IDE sensor was fabricated by thermal vacuum evaporation. Aluminum (Al) was used as an electrode material. The sensing substrates upon which the PANI nanoparticles films was deposited consisted of an Al electrodes 0.25 mm wide with 0.51 mm gap each 10 mm long on a polyethylene terephthalate (PET) substrate. Then, PANI nanoparticles was deposit by inkjet printing method onto the Al tracks of the sensing substrate. PANI nanoparticles was synthesized by chemical polymerization dispersion of corresponding monomers as an active sensing layer. Dodecylbenzenesulfonic acid (DBSA) was used as a dopant material, ammonium peroxydisulfate (APS) as an oxidant material and sodium dodecyl sulfate (SDS) as surfactants compounds.

Particles size of PANI nanoparticles was measured by Mastersizer 2000, while the UV-Visible spectra analysis of the synthesized PANI nanoparticles was analyzed by UV-vis spectroscopy. Optical microscopy and Scanning Electron Microscopy (SEM) was used to investigate the morphology of PANI nanoparticles thin film. Fourier Transform Infrared Spectroscopy (FTIR) analysis was carried out for identifying chemicals compounds that are either organic or inorganic. IDE sensor for methanol vapour was analyzed to determine the effect of thickness, response time, recovery time, repeatability, sensitivity, selectivity, reproducibility and shelf life (lifetime) of sensor as sensor characteristics.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter explains the background study in this research. Chapter 2.2 reviews the general conducting polymer (CP) include synthesis and deposition method of CP. Chapter 2.3 describes about polyaniline, route to synthesis PANI conventionally or in nanoparticles, and mechanism of detection. In chapter 2.4 the inkjet printing method and effect of deposition thickness is explained. The configuration of IDE is explained in chapter 2.5. Chapter 2.6 includes the classification, characteristics, and an utilization of CP as gas sensor.

2.2 Conducting Polymers

Conducting polymers (CP) are a group of conjugated polymers that exhibit excellent electrical conductivity. It is belong to a novel class of materials that are being evaluated for application in charge storage devices (batteries or capacitors), electromagnetic screens, sensors, membranes and corrosion protective coatings (Jude, 2002). Most of the commercially available sensors are made from metal oxides and it operate at higher temperature. In comparison with that the sensor made from CP has many improved characteristics such as higher sensitivity, short response time, and operate at room temperature. As a result, tremendous efforts have been gave towards the development of electrochemical and gas sensors made from CP (Shrivas et al., 2008).

CP are easy to be synthesized through chemical or electrochemical processes, and their molecular chain structure can be modified conveniently by copolymerization or structural derivations. Figure 2.1 show that some common CP used in gas sensor (Bai & Shi, 2007). However, the conductivity of these pure CP are rather low (<10^{-5} S cm^{-1}). In order to achieve highly CP, doping process is necessary. The concept of doping is the central theme which distinguished CP from all other polymers (MacDiarmid, 2001). It can be doped by redox reaction or protonation and oxidation process. The protanation reaction is only applicable to polyaniline (PANI).

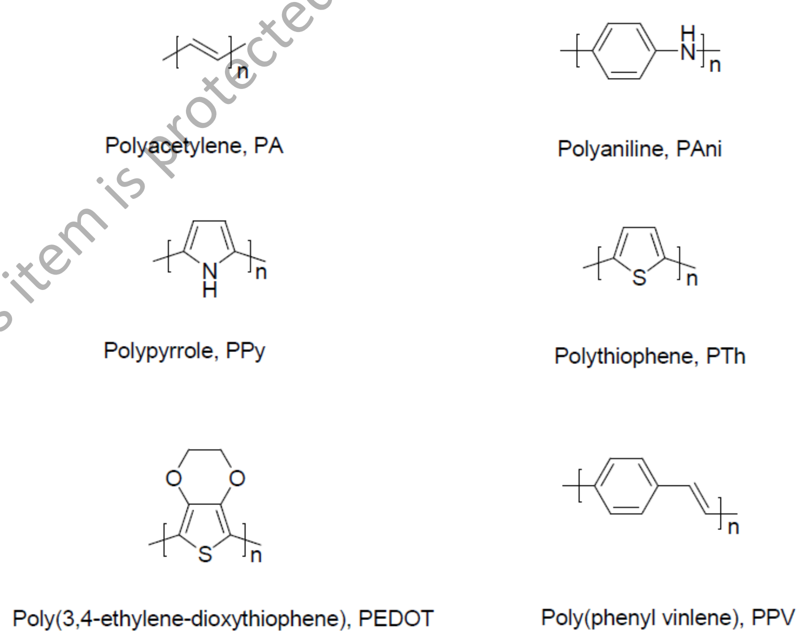

Figure 2.1 Some common conducting polymers