

Wireless Graphene Nanowires QCM Ethanol Vapor Sensor Network Based on ZigBee Protocol

Jiaping Liao, Yang Lu, Xiaohua Wang*, Ding Qian, Rujiao Cheng and Dongli Zhu

Department of Electrical Engineering, East China Normal University, 500 Dongchuan Road, Shanghai 200062, PR China

Abstract—In this paper, a ZigBee wireless ethanol vapor sensor system has been presented. This system is based on quartz crystal microbalance (QCM) coated with graphene nanowires as sensing element. This system is a QCM ethanol vapor sensor network, and we use star network to construct it. It consists of two parts: one is the sensor transmitter module with consist of lots sensor transmitter; the other is a network center. Every sensor transmitter is a ZigBee coordinator linked with grapheme-nanowires-modified QCM ethanol vapor sensor, and it is responsible to acquire information from QCM sensor and transmit information to network center. The network center constructed with ZigBee coordinator also but linked with computer, and it is responsible to processing and controlling. It is indicated from experimental results that the stability, sensitivity and reproducibility of this wireless sensing system are quite good. The proposed system is low-cost and real-time, and it can not only be used to monitor ethanol vapor but also detect the polluted gas in family and harsh environment.

Keywords- QCM(quartz crystal microbalance) sensor; ZigBee; graphene nanowires; sensor network

I. INTRODUCTION

Volatile organic compounds' detection has turned the earth interest in the past few decades, because of worries about human health care, environmental protection, quality control and industrial processing. Moreover, growing attention has been paid on the accidents that were caused by car drivers and people operating complex facilities with their judgment harmed by ethanol. The online detecting of the ethanol vapor is an significant job, Because the accidents are not only a risk to themselves but also affect others' safety. A quantity of sensors have been developed, they are not only for drunken drivers but also for environmental protection, quality control application and so on. [4]

Quartz Crystal Microbalance (QCM) gas sensor is widely used both in industry and in daily life, particularly in food yield (detecting and handling the process of the food yield), in chemical plant (discovering the venomous gas and the flammable gas), in the environmental protection (detecting and handling the polluted gas), in identifying the gas (ethanol vapor, ammonia, and so on). It is widely used in biomedicine primarily for the reason that it can identify the gas produced by the organism. The way to diagnose the disease through observing the gas that was breathed from the body has been paid grand attention these years. QCM can be using in wireless senses system easily through linking ZigBee coordinator owing to its digital characteristics. [2][3]

Graphene have been received exceptional attention because of its high electrical conductivity and remarkable nanostructure in recent years[7][8]. The graphene metal oxide composite film with high electrocatalytic activity and high electrical conductivity will give great promise for the construction of novel nonenzymatic biosensors[5]. In this paper, a fresh QCM sensor was presented for ethanol vapor's determination. The QCM sensor was coated with graphene nanowires as sensing element.

Wireless sensor network consists of lots nodes. These nodes are low cost, small volume and have the capable of wireless communication and data processing. In wireless sensor networks, a large number of sensor node distributions in the whole monitoring area, each sensor node will detected the useful information and transmit it to the user. The data transfer process is realized through adjacent nodes relay transmission, eventually transferred to the control center. At present, several short-range wireless network technology are becoming focus of the industry, they are wireless LAN(Wi-Fi), ultra wideband communication(UWB), near field communication (NFC), Bluetooth, infrared data communications (IrDA) and ZigBee technology. [11]

In many wireless network technologies, wireless network technology based on ZigBee with low power consumption, low cost, low complexity features loved by an increasing number of businesses and individuals of all ages. ZigBee is a low-power LAN protocols based on IEEE802.15.4 standard. ZigBee protocol from bottom to top respectively are the physical layer (PHY), media access control layer (MAC), transport layer (TL), network (NWK) layer, application layer (APL), etc. The physical layer and the media access control layer are follow the IEEE 802.15.4 standard rules. Zigbee technology is particularly suited for these occasions: small data throughput, small network construction investment, higher requirements of the network security, inconvenience frequent battery replacement or recharging. It is expected to be widely used in consumer electronics equipment, intelligent household, industrial control, medical equipment control, agricultural automation fields, etc. [9][10]

In this paper, a wireless ethanol vapor sensor network was developed through combining the QCM sensor technology, the microcontroller technology and the ZigBee RF wireless technology. It can be applied to large number of fields, such as monitoring the combustible gas and the venomous gas, environmental protection, biomedicine etc.

II. SYSTEM ARCHITECTURE

A. System Description of the Wireless Sensor Network

There are three network topology types in IEEE 802.15.4, star structure, grid structure and family structure. As show in FIGURE I.

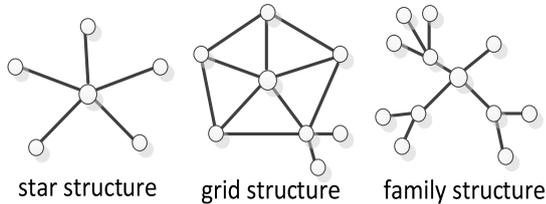


FIGURE I. NETWORK TOPOLOGY TYPE OF IEEE 802.15.4

For star structure is simple and easy to set up, so we choose star structure as the network topology of our ethanol sensor system. Obviously, there are two node types in star structure, the center node and the terminal node. Center node connects to PC and gathers information from terminal node. And terminal nodes connect to sensor.

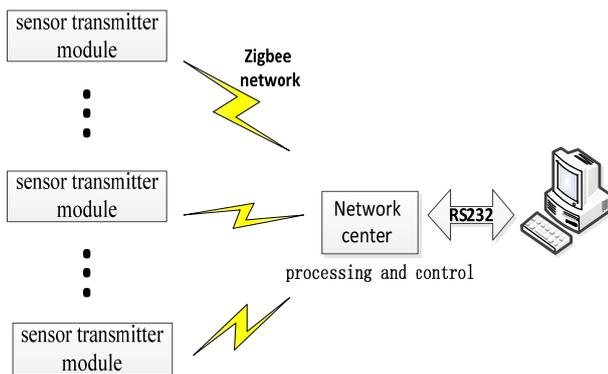


FIGURE II. THE SCHEMATIC DIAGRAM OF WIRELESS ETHANOL VAPOR SENSOR SYSTEM

The schematic diagram of wireless ethanol vapor sensor system is shown in FIGURE II. The wireless sensor network consists of two main parts, called the network center and the sensor transmitter module. For CC2530 chip with the function of RF (radio frequency) itself, so it don't need additional RF chip for the design of ZigBee network node. The CC2530 chip with some simple circuit can realize the function of RF. So we use CC2530 chip in all ZigBee network nodes.

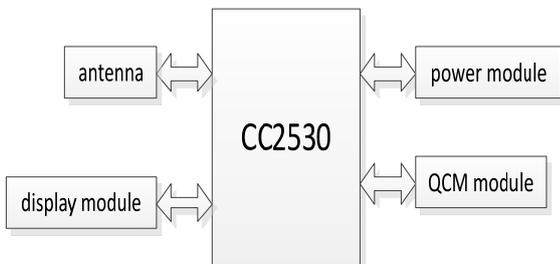


FIGURE III. THE SENSOR TRANSMITTER MODULE'S DIAGRAM

The sensor transmitter module's diagram is shown in FIGURE III. The sensor transmitter module is used to monitor the ethanol vapor and transmits the information of sensor to the network center. The ZigBee coordinator is connected to QCM sensor that was coated with grapheme nanowires. The oscillating circuit of QCM which drives the quartz crystal is constructed by a TTL inverter chip 74HC04. The QCM's oscillation frequency is gauged by a software frequency counter that was implemented through CC2530 chip. The oscillation frequency transmitted to the network center by ZigBee protocol.

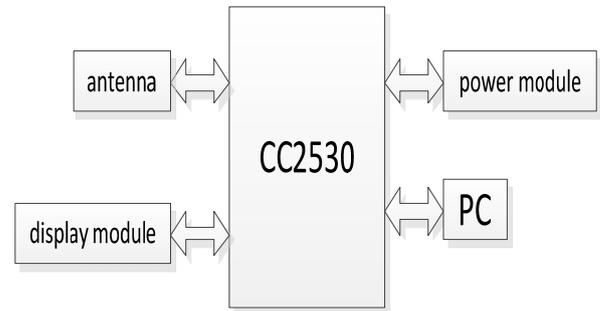


FIGURE IV. THE NETWORK CENTER'S DIAGRAM

The network center's diagram is shown in FIGURE IV. It consists of a ZigBee coordinator, power module, display module and PC. Zigbee coordinator is constructed with CC2530 chip as MCU block and RF block. The PF block is bases on ZigBee protocol and operates at 2.4GHz. The MCU block is responsible to processing and control. Different with the sensor transmitter module, the ZigBee coordinator is connected to PC, and transmits information to PC via RS232 (serial) communication protocol. The center network is used to record and analyze the sensing information transmitted from the sensor transmitter module.

The ZigBee node's photograph is shown in FIGURE V. It is employed both in the network center and the sensor transmitter module.



FIGURE V. THE PHOTOGRAPH OF THE ZIGBEE NODE

B. Apparatus for Gas Sensing Application

We designed a gas sensing system to examining the effective of the wireless sensing system, it was pictured in

FIGURE VI. It includes sensing chamber with QCM, sample gas inlets with valves, a mass flow meter, ZigBee coordinator for data acquisition and analysis. As the QCM is also sensitive to the velocity of flow, particularly when the concentration is quite low (<10 ppm), a mass flow meter controller is used to limit the flow to a certain rate. The examination results do not generally relate to the flow rate in the range of 50-300 ml/min if only the flow stays constant during the experiment. The chamber in FIGURE VI is not all right. Though the experimentation was executed in nitrogen environment the experimentation environment is very close to the real ambient air.

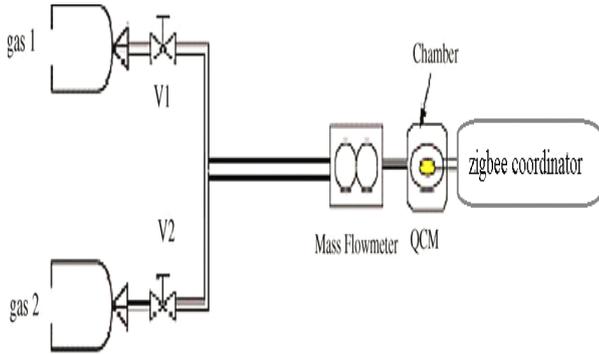


FIGURE VI. BLOCK DIAGRAM OF TESTING SYSTEM[1]

C. Sensor Configuration[6]

The sensor with graphene nanowires as the sensing materials that were started from 8 MHz AT-cut polished quartz crystal (International Crystal Manufacturing Co.Inc., Oklahoma City, OK, USA) with gold and wafer electrode of 5.1mm and 14, respectively. The crystals with gold electrodes were first cleaned carefully with the acetone, IPA, and DI water and dried with N₂. The corresponding resonant frequencies were recorded as the references.

The graphene nanowire-contained ethanol solution was the applied to the surface of crystals through dropcoating technique. The crystals were placed horizontally to make sure a uniform thin film distribution. Thereafter, the crystals were placed at 100 centigrade for 20 min to ensure the ethanol volatilizing completely and the thin film formation. This could be confirmed by the fact that no further frequency shift is observable. The frequency shifts were measured to evaluate the thickness of the coated layers that were based on Sauerbrey equation:

$$\Delta f = -2.26 \times 10^{-6} f^2 \Delta m / A \quad (1)$$

where f (MHz) is the fundamental frequency of the unloaded piezoelectric crystal, Δm (g) the mass loading on the surface of the crystal and A (cm²) is the surface area of the electrode. Up to now, according to our knowledge there is no report about the accurate model to compute the density of the nanowires in this morphology, but the density is only a relative physics parameter in our experiment.

III. EXPERIMENTAL PROCEDURE

A. QCM Ethanol Vapor Sensor Network Constructed

Before monitoring the ethanol vapor, communication between the sensor transmitter module and the network center should be fabricated. The sensor transmitter will send the frequency of QCM to the network center, and then the data will be recorded by the computer. The distance between the sensor transmitter module and the network center is from 5m to 100m. The different distance will not lead to different consequences.

B. Detecting Ethanol Vapor

After sensor network fabricated, the examination goes following the two steps below. Before a examination is begun, 150 ml/min nitrogen was drove through the chamber (approximately 15 ml) till the QCM frequency change rate smaller than 0.1 Hz/10 s. In this state, we say QCM achieves a balance. This process usually takes about 20 min. The gas for testing is then used to this measurement system at the same temperature and the flow rate is also the same with previous step. When the QCM achieves a new balance, the examination is over and a new examination may begin from this new balance if the background atmosphere is the same. About 90s is cost by this step. Ethanol vapor's concentration is then calculable according to the frequency changes between the testing gas and background atmosphere. All the processes were taken under room temperature and at controlled humidity environment.

IV. RESULTS AND DISCUSSIONS

A. Stability of the Wireless Alcohol Vapor Sensing System

In this experimentation, the QCM sensor only worked at nitrogen environmental and sent the stability data through ZigBee protocol to the computer, you can see the result in FIGURE VII. Here, the stability is referred to graphene nanowires-coated QCM's resonant frequency change with the processing time. All graphene nanowires-coated QCM sensors kept the nice frequency stability. All the sensors working in air, as shown in FIGURE VII, the frequency shifts was less than -10 Hz within 1min. So following the method in part 2.3, the graphene nanowires' thickness is calculable according to the frequency shifts in FIGURE VII.

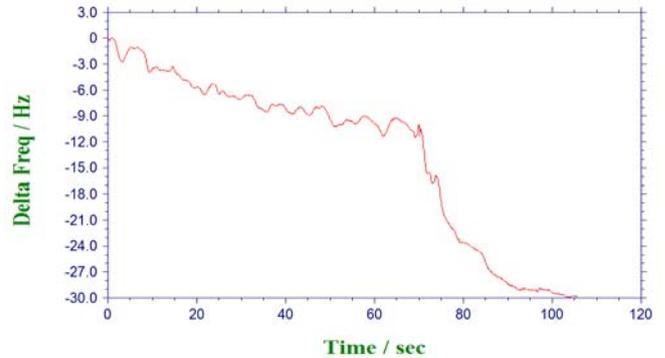


FIGURE VII. TIME-DEPENDENT OF THE COATED SENSOR WORK IN NITROGEN ENVIRONMENT AT ROOM TEMPERATURE

B. Characteristics of the Sensor

The sensor's time-cycling response is shown in FIGURE VIII. The experimentation was repeated over 30 times and sensors with different graphene nanowires thickness have the same response. This showed that the sensor worked in a reproducible manner. No other response was observed. Moreover, the frequency decreased due to ethanol vapor's adsorption to graphene nanowires-modified electrode's surface according to Eq(1). And the crystal' frequency back-shifts to its initial value due to ethanol vapor's full desorption from the electrode surface. The way to full desorption is purging nitrogen through the chamber. The phenomenon proved that the electrode was sensitive to ethanol vapor. As shown in FIGURE VIII, the wireless ethanol vapor sensor system works well and it can be used as real-time-monitoring ethanol vapor sensor system.

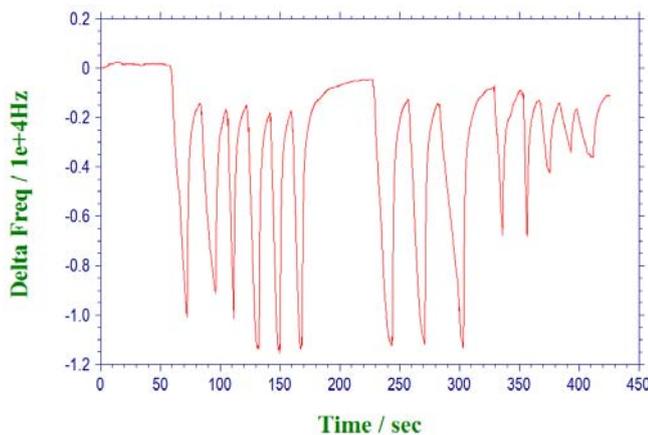


FIGURE VIII. THE TIME-CYCLING RESPONSES OF THE WIRELESS SENSOR

V. CONCLUSIONS

Wireless QCM ethanol vapor sensor system that was based on ZigBee protocol was constructed and studied in this paper. A number of issues such as accuracy, reproducibility and stability of this sensor system had been discussed. It is concluded that the QCM coated with graphene nanowires can enhance some sensor performance like the response time and the sensitivity and can make on-line detection possible for the real time. The wireless ethanol vapor sensor system that is developed can apply in the sensor network application or chemical sensor in the environment detection.

REFERENCES

- [1] Honghu Huang, Jia Zhou, Shengyu Chen, Lei Zeng, Yiping Huang, A highly sensitive QCM sensor coated with -ZSM-5 film for medical diagnosis, *Sens. Actuators B* 101 (2004) 316-321
- [2] X. Wang, J. Zhang and Z. Zhu, *Appl. Surf. Sci.* 2404, 252 (2006)
- [3] X. Wang, Y. Ding, J. Zhang, Z. Zhu, S. You, S. Chen and J. Zhu, *Sens. Actuators B* 421, 115 (2006)
- [4] Huihui Guo, Xiangdong Chen, Yao Yao, Guangtao Du, Hui Li, Detection of ethanol and methanol vapors using polymer-coated piezoresistive, *Sensors and Actuators B* 155(2011)519-523
- [5] Li-Ping Jia, Huai-Sheng Wang, Preparation and application of a highly sensitive nonenzymatic ethanol sensor based on nickel

nanoparticles/Nafion/grapheme composite film, *Sensors and Actuators B* 177(2013)1035-1042

- [6] Xiaohua Wang, Jian Zhang, Ziqiang Zhu, Ammonia sensing characteristics of ZnO nanowires studied by quartz crystal microbalance, *Applied Surface Science* 252(2006) 2404-2411
- [7] S. Gilje, S. Han, M. Wang, K.L. Wang, R.B. Kaner, A chemical route to graphene for device applications, *Nano Letters* 7 (2007) 3394-3398
- [8] S. Stankovich, D.A. Dikin, G.H.B. Dommett, K.M. Kohlhaas, E.J. Zimney, E.A. Stach, R.D. Piner, S.T. Nguyen, R.S. Ruoff, Graphene-based composite materials, *Nature* 442 (2006) 282-286
- [9] PIC18F4620 DataSheet CC2420 2.4 GHz IEEE 802.15.4/ZigBee-ready RF Transceiver
- [10] IEEE 802.15.4, Part 15.4: Wireless Medium Access Control(MAC) and Physical Layer(PHY) Specifications for Low-Rate Wireless Personal Area Network (LR-WPANs). October 2003
- [11] Mohammad Ilyas, Imad Mahgoub, *Handbook of Sensor Networks: Compact Wireless and Wired Sensing Systems*, CRC press. USA. 2005