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# Fabrication of a sensor array based on quartz crystal microbalance and the application in egg shelf life evaluation

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ABSTRACT

In this study, a QCM sensor array with four different surface modified QCM sensors (i.e., multi-walled carbon nanotubes, graphene, copper oxide and polyaniline) was fabricated and was applied to evaluate the shelf life of eggs by sensing the volatiles. The morphologies of the sensitive materials on electrodes were analyzed by field-emission scanning electron microscope (FE-SEM), and sensor responses were monitored by a self-made frequency measurement system. Particularly, these four sensors exhibited relatively good sensitivity, reversibility, repeatability and long-term stability. Then, the sensor array was applied to detect volatiles of eggs with different shelf life. The result of linear discriminant analysis (LDA) outperformed principal component analysis (PCA), and exhibited excellent classification accuracy. Partial least square regression (PLSR) was employed to predict the shelf life of eggs and the fitting coefficient of determination ($R^2$) of PLSR increased from 0.8474 to 0.9547 after kernel principal component analysis (KPCA) introduced, which showed satisfactory prediction performance. It could be concluded that the QCM sensor array is effective for the detection of eggs with different shelf life, offering an alternative strategy to estimate the freshness of eggs.



## 1. Introduction

Egg plays an increasingly indispensable role in our daily diet for its high protein and rich nutrients. Because the thick and fragile eggshell hinders the inner quality detection of eggs, one of a major concern in egg industry is to determine the freshness of eggs in an efficient and nondestructive way. Traditionally, the quality evaluation of eggs depends on visual inspection, it is subjective and inefficient. The assessment of quality parameters such as Haugh unit, yolk factor, the size of air cell and the thickness of eggshell, etc., are precise but destructive [1]. Some instrumental analytical method such as gas chromatography–mass spectroscopy (GC–MS) is widely used in detecting physicochemical indexes of eggs [2]. However, it often takes considerable time and complex procedures to prepare samples, thus making online detection difficult. Machine vision and acoustic impulse methods are also commonly used to classify eggs by appearance or to estimate eggshell defects [3,4], which ignore the change of internal quality. Visible spectroscopy/near infrared spectroscopy (VIS-NIRS) is a rapid and nondestructive approach [5,6], but it cannot evaluate the internal quality of eggs directly and might be affected by eggshell or environmental factors.

To achieve a nondestructive and effective evaluation of eggs' freshness, an alternative strategy is to detect the volatiles emitted from whole egg by using gas sensors. With the increase of storage time, the composition and content of the internal compounds of eggs changed, which correspondingly leads to the change of volatiles. Eggs are rich in proteins, lipid, and carbohydrates. With the storage time increasing, these nutrition may be decomposed by microorganisms and produced ammonia, amine, sulfide, aldehydes, ketones, alcohols and other compounds. The microporous structure of the eggshell allows the internal volatiles compounds to come out, which provides direct information about the internal quality of eggs. Researches have proved the possibilities of evaluate eggs' quality by gas sensors [7,8].

Among various kinds of gas sensors, resistance sensitive gas sensors based on metal oxide semiconductor (MOS) have been widely used in quality evaluation of foodstuffs, such as meat, fruit, and milk in form of a sensor array. Nevertheless, most of the metal oxides have relatively low sensitivity at room temperature. They reach desirable sensitivity at approximately 300–400 °C, resulting in high operating temperature and high power consumption.

Given that circumstance, quartz crystal microbalance (QCM) has received more attention recently in the field of gas sensing because

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of its high sensitivity, facile operation and low working temperature [9,10]. QCM gas sensor is a mass sensitive sensor, and the principle of sensing in gas phase was demonstrated by Sauerbrey equation, which establishes a linear relation between the change of resonance frequency and the change of mass on the electrodes. By measuring the resonance frequency changes caused by adsorption, nano gram-level of mass change can be detected, and the information of gas samples can be easily obtained.

To enhance the sensitivity of the sensors, different functional materials are employed to modify the surface of the quartz crystal. Metal oxide semiconductor [11], carbonic material, nanostructured material, polymers [12,13] and hybrid material are commonly utilized surface modification materials. Metal oxide semiconductor materials are reported to have high affinity for aldehydes, alcohols and ketones [14]. Conducting polymers also have been widely used in gas detection due to their conductivity and facile synthesis [15,16]. Carbonic materials such as graphene [17–19] and carbon nanotubes [20] are widely studied because of their large surface area and excellent conductivity. Nanostructured sensitive materials exhibit enhanced sensibility owing to their enlarged specific surface area [21]. These functional materials highly improve the gas sensing properties of QCM sensors.

Because of the advantages mentioned above, single QCM sensor has been applied in detecting various kinds of vapors [22], for instance, volatile organic compounds [23–26], humidity [27,28], and chemical agents [29,30], etc. Although single QCM sensor has been widely used in vapor detection, there were few reports on food quality evaluation based on QCM sensor array. No known researches have been reported to evaluate the shelf life of eggs based on QCM sensor array.

In this study, a QCM sensor array with four sensors was developed for the shelf life evaluation of eggs. To improve the cross sensitivity and eliminate the correlation of the sensor array, four different kinds of sensitive materials were chosen for the surface modification of the four sensors, which are carbon nanotubes (CNTs), graphene, copper oxide (CuO) and polyaniline (PANI). The main purposes of this study are: (1) to fabricate QCM sensors with good sensing properties by using proper surface modification methods, (2) to characterize the sensitive films deposited on the QCM sensors and test the gas sensing properties such as sensitivity, reversibility, repeatability, selectivity and long-term stability of the QCM sensor array, (3) to discriminate eggs with different shelf life and to predict the shelf life of eggs with the fabricated QCM sensor array.

## 2. Material and methods

### 2.1. Modificaiton of QCM sensors

#### 2.1.1. Sensitive materials

According to literatures, there were various volatiles in whole eggs. Literature [31] found that the concentration of 3-ethyl-2,5-dimethyl-pyrazine, benzothiazole and sulfide compounds contributed most to the aroma changes during storage. Literature [32] illustrated that methyl sulfide compounds were directly related to deterioration and perception of unacceptable odors in whole eggs. Besides, there were ammonia, amine, aldehydes, ketones and alcohols in volatiles of rotten eggs. Based on the volatiles profile in eggs, four different kinds of sensitive materials were chosen for the surface modification of four sensors, which were carbon nanotubes (CNTs), graphene, copper oxide (CuO) and polyaniline (PANI).

Copper oxide is a typical metal oxide semiconductor material, which is reported to have higher affinity for hydrogen sulfide [33]. Polyaniline is one of the most common conducting polymers, which shows better sensitivity to ammonia [34]. Graphene and carbon nanotubes are carbonic material, which have high specific surface area and high sensitivity to amine and alcohols [35]. These four different materials belonged to different categories of sensitive materials, which could enhance cross sensitivity and eliminate correlation of the sensor array.

#### 2.1.2. Chemicals and reagents

The AT-cut 8.98 MHz ± 30 kHz quartz crystals with Au electrodes were purchased from Ametek Inc, Shanghai, China, and the diameter of the electrode is 5 mm. The main chemicals and reagents used in this research are as follows. Multi-walled carbon nanotube, graphene, copper oxide and aniline were purchased from Aladdin Industrial Corporation. Poly diallyl dimethyl ammonium chloride solution (PDDA, Mw < 100,000, 35 wt%) and poly(styrene sulfonic acid) sodium salt(PSS, Mw < 70,000) were also purchased from Aladdin Industrial Corporation. All chemical reagents were analytical grade and were used without further purification.

#### 2.1.3. The fabrication of QCM sensors

A typical procedure to fabricate QCM sensors was as follows. Firstly, the prepared QCM sensors were treated with piranha solution (30% $H_2O_2$: 98% $H_2SO_4$ = 1:3, v/v) for 2 min to add hydroxyl groups and carboxyl groups on surface of electrodes, and then rinsed with deionized water and dried in $N_2$ atmosphere at room temperature. Secondly, each quartz crystal was decorated with 3 bilayers of PDDA and PSS by alternately dipping into 2 wt% of PDDA and 2 wt% of PSS aqueous solution for 3 times. After each dipping process, the crystal was rinsed with deionized water and dried in $N_2$. After that, four 0.01 g/L solutions were prepared by dissolving carbon nanotube, graphene, copper oxide and PANI, respectively, into DMF solutions. Then, four quartz crystals were modified by dipping into the prepared solution respectively, and each dipping process lasted for 3 min, ensuring that both electrode surfaces of QCM were covered with sensitive materials uniformly. After deposition, the sensors were dried in vacuum at 50 °C for 12 h, then single layer modified QCM sensor were obtained. Repeating the deposition procedure for several times and multi-layer modified sensor was obtained.

### 2.2. Measurement setup and procedures

#### 2.2.1. Measurement setup

A self-made frequency monitoring system was used in this experiment. It consists of four modified quartz crystal microbalance sensors, a piece of quartz oscillator circuit, a frequency counter device and a compatible computer. The oscillator circuit was consist of resistances, capacitances and operational amplifiers, which could oscillate four quartz crystals at the same time and generate periodic signals. The frequency counter, which had four channels, was designed by using field programmable gate array (FPGA) to monitor the resonance frequency of the sensors during gas sensing process and send frequency data to computer via RS-232 serial communication port. A LabVIEW software was programed as the main controller, capable of receiving data from the frequency counter, processing signal, displaying sensor response curves and recording data. The resolution of the frequency monitoring system was 0.1 Hz, and the measuring range is from 1 Hz to 100 M Hz. The time interval of frequency counter was configured to 1 s.

The experimental setup was shown in Fig. 1. Four QCM sensors were set in a sealed chamber made of Teflon with a volume of 500 mL. All sensors were oscillated by oscillator circuit, and connected to the frequency counter. The frequency shifts of the sensor array were measured and processed by frequency counter and were sent to PC. There were an inlet and an outlet on the test chamber for carrier gas nitrogen going in and out. A small elastic bag was intro-