

Analytical Performance and Characterization of a Quartz Crystal Microbalance for the Detection of Cu(II) Ions in Water

Chi-Yen Shen¹, Roan Yeh¹, Mei-Hui Chung², Rey-Chue Hwang^{1,*}

¹Department of Electrical Engineering, I-Shou University, Kaohsiung, Taiwan

²Office of Library and Information Services, I-Shou University, Kaohsiung, Taiwan

Email address:

cysen@isu.edu.tw (Chi-Yen Shen), popokago0306@gmail.com (Roan Yeh), mhchung@isu.edu.tw (Mei-Hui Chung),

rchwang@isu.edu.tw (Rey-Chue Hwang)

*Corresponding author

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Abstract: A novel quartz crystal microbalance (QCM) sensor based on combining phosphate-modified dendrimer and ionophore has been developed for the determination of Cu(II) ions. The performance of the developed QCM sensor was evaluated based on frequency data and experimental results evidently indicated that the prepared sensor could be sensitive for the determination of Cu(II) ions in water. The obtained QCM sensor presents good selectivity monitoring of Cu(II) ions, short response time (40 s), and wide linear range (0.01-100 μ M).

Keywords: Quartz Crystal Microbalance, Metal Ion, Sensitivity, Selectivity

1. Introduction

The quartz crystal microbalance (QCM) is a well-established tool in mass-sensitive detection. These devices typically consist of an AT-cut quartz crystal with electrodes patterned on opposite sides. An electrical field, applied to the QCM, produces mechanical stresses that induce acoustic wave to travel in a direction perpendicular to the surfaces of the crystal. Therefore, QCM that can be electrically excited into a shear mode of vibration could be used to probe interfacial processes on quartz surface.

The QCM can consequently detect mass changes due to these molecular interactions on the surface of the QCM. The potential of QCMs for chemical sensor was an application of the Sauerbrey [1], who first described the relationship between the frequency shift and mass change on the crystal surface in air. The Sauerbrey equation is defined as:

$$\Delta f = -\frac{2f_o^2 \Delta m}{A(\rho_q \mu_q)^{1/2}} \quad (1)$$

where Δf is the measured frequency shift, f_o is the

fundamental resonant frequency, Δm is the mass change due to surface deposition, A is the piezoelectrically active crystal area defined by the two gold electrodes, ρ_q is the density of quartz crystal and μ_q is the shear modulus. Eq.1 is developed for oscillation in air and only applies to rigid masses attached to the crystal. It is applicable to only gas phase mass deposition. If the solution passes over the QCM crystal surface, the frequency response of the QCM is dependent on bulk liquid properties such as conductivity, viscosity, density and dielectric constant [2, 3]. The Kanazawa and Gordon's equation describes the oscillating frequency in liquid phase as follows:

$$\Delta f = -f_o^{3/2} \left(\frac{\eta_l \rho_l}{\pi \rho_q \mu_q} \right)^{1/2} \quad (2)$$

where ρ_l is the density of the liquid and η_l is the viscosity of the liquid. The QCM device is convenient to use and could rapidly detect real-time responses of chemical interactions on the surface of device [4, 5]. Therefore, the low cost and easy operated QCM device has been applied in various biotechnology and chemical fields, such as clinical diagnosis [6-8] and environmental monitoring [9]. In this study, a

simple QCM-based liquid sensor was developed to monitor metal ions without complex procedures. The efficiency, sensitivity and selectivity of the sensor were also evaluated to further enhance its practicability in drinking water.

Heavy metals are naturally occurring elements that have a high atomic weight and a density at least 5 times greater than that of water [10]. Several factors including the dose, route of exposure, and chemical species influence the degree of toxicity. The overall toxicity also depends on the age, gender, genetics, and nutritional status of exposed individuals. Among heavy metals, arsenic, cadmium, chromium, lead, and mercury reduce significant health risks due to their high degree of toxicity. These metallic elements are considered systemic toxicants that are known to induce multiple organ damage, even at lower levels of exposure [10].

The multiple applications in industry, agriculture, medicine, and technology widely use chemical products to result in a wide distribution of chemicals in the environment. These results raise concerns over potential effects of chemicals on human health and the environment [10–12]. Therefore, the detection of heavy metals in aqueous environments has attracted wide attention in recent years. Detection and quantification of heavy metals have been investigated by utilizing atomic absorption spectroscopy [8, 9], high performance liquid chromatography [10, 11], inductively coupled plasma-mass spectrometer [12, 13], and anodic stripping voltammetry [14]. However, such analytical methods have been found to have practical limitations with respect to cost, complexity and the requirement for a well-trained operator. Therefore, a variety of rapid, sensitive sensor has been developed for detecting metal ions in order to overcome these limitations. Many kinds of sensors have been studied for heavy metals determination, such as electrochemical sensors [20] and biosensors [21].

In this study, detection of Cu(II) ions in water has been investigated. Among heavy metal ions, copper has become a widely distributed pollutant in natural water as a result of the dumping of electronic trash and mining residues [21]. On the other hand, Cu(II) is the third most abundant transition-metal ion in the human body and is essential for the biochemical and physiological functions [22]. Its deficiency and excess lead to malfunction of the liver, heart diseases, neurological disorders, and deterioration of connective and bone tissues [10].

Dendrimers are branched polymers with well-defined sizes and geometries. Dendrimers with multiple surface functional groups are a new attractive class of macromolecules [23–25]. The ability of dendrimers to coordinate metal ions in their interior branches or in their exterior units can be exploited to develop sensors of high selectivity and sensitivity. The structural features of the multiple branches provide many active sites, which can bond with targets at many points. In addition, phosphate anions can exhibit high affinity for various types of metal ions and have been applied for ion sensing [26, 27]. *o*-Xylylenebis (N,N-diisobutyldithiocarbamate) is copper(II) ionophore I and forms chelates with copper of high stability as compared to other metals. Hence, taking these

advantages into consideration, we designed and synthesized a new film of phosphate-modified dendrimer (A) incorporating PVC based on copper(II) ionophore I (B) as a sensing membrane. In this paper, a QCM sensor coated with this new membrane has been developed for the detection of Cu(II) metal ion in water. The detection responses of sensor on Cu(II) metal ion sensing performance were studied quantitatively.

2. Experimental Methods

2.1. Reagents

All reagents were of analytical reagent grade and were used without further treatment. PAMAM dendrimer (ethylenediamine core, G5), polyvinyl chloride (PVC), tetrahydrofuran (THF), and copper(II) ionophore I were purchased from Sigma–Aldrich, USA. Dimethylformamide (DMF) and phosphoric acid were obtained from Fluka and Kojima Chemical Co., Japan, respectively. All aqueous solutions were prepared with doubly deionized, distilled water.

2.2. Preparation of Sensing Membrane

100 μ L of 5 wt% PAMAM dendrimer (ethylenediamine core, G5), whose chemical structure is shown in Figure 1, was dispersed in 900 μ L of 30% phosphorous acid solution in an ultrasonic bath for 7.5 h to produce phosphate-modified dendrimer (A) and then rinsed by deionized water. 1 mg copper(II) ionophore I was dissolved in 50 μ L of THF and was agitated in an ultrasonic bath for 30 min. 0.1 g PVC was dissolved in 4.8 mL of DMF and was agitated in an ultrasonic bath for 20 min. Then, the mixture of 1 mL PVC solution and 50 μ L ionophore solution was agitated in an ultrasonic bath for 1 h to produce PVC based on copper(II) ionophore I (B). The ion selective membrane solution was obtained mixing materials A and B at a specific ratio in an ultrasonic bath for 30 min.

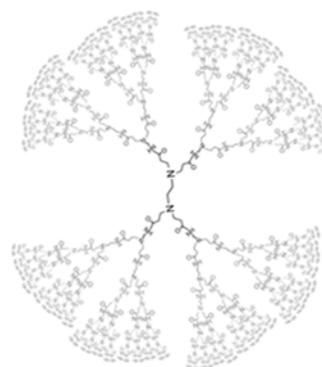


Figure 1. Chemical structure of ethylenediamine core G5 PAMAM dendrimer.

2.3. Preparation of the QCM Sensor

The QCM device (Taitien Co., Ltd, Taiwan) with an operation frequency of 10 MHz was used in this work. QCM samples were first cleaned with piranha solution for 30 s. A

drop of 5 μL sensing membrane solution was dropped on the electrode surface of each QCM sample at room temperature. Then the QCM samples were dried in a vacuum oven at 80°C. Finally, the samples were rinsed again with deionised water and dried with N_2 gas.

The fabrication procedure of a QCM sensor based on ion selective membrane is illustrated in Figure 2 and a real image of a sensing membrane coated QCM sensor is shown in Figure 3.

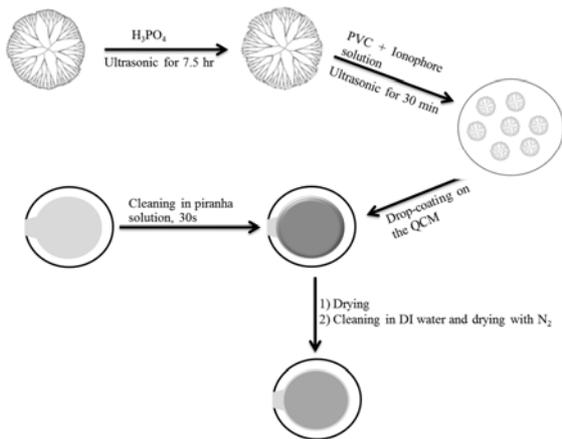


Figure 2. Schematic of the fabrication procedure of a QCM sensor.



Figure 3. A photograph of a QCM sensor.

2.4. Apparatus

An apparatus shown in Figure 4 was used to monitor metal ions in this study. A counter (53131A, Agilent, USA) measured oscillation frequency of the QCM device. A computer through a GPIB interface controlled the counter, and the software for taking measurements was designed by LabVIEW 8.6 (National Instruments, USA). Figure 5 shows that a QCM sensor was mounted by concentric rubber seals into a flow cell to provide contact with only one side of the quartz crystal to the liquid. Solutions were injected into the flow cell by two syringe infusion pumps (KDS 200, KD Scientific Inc., USA), through 0.5mm diameter silicon tube for liquid exchange, as shown in Figure 4. The cell was shielded with a temperature controller box that was

maintained at 20°C.

The QCM sensor was designed to make use of the Pierce oscillator circuit plotted in Figure 6 to generate the oscillation in this study. The design of a crystal-controlled oscillator used as a QCM sensor in liquid is a difficult task because of the wide dynamic values of the resonator resistance that they should support during their operations [28]. The QCM experiences a large reduction in its quality factor that caused by the liquid. The Pierce oscillator design provides a great stability in frequency and a low phase noise. Output spectrum of the QCM oscillator measured by the spectrum (Model 4395A, Agilent, USA) is shown in Figure 7 and indicates QCM generated stable oscillation occurred at 10 MHz.

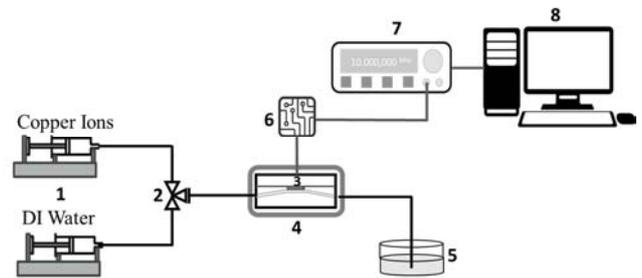


Figure 4. Diagram of the experimental system: 1: syringe pumps; 2: flow valve; 3: QCM; 4: temperature-controlled flow cell; 5: waste; 6: oscillator circuit; 7: frequency counter; 8: computer.



Figure 5. A QCM sensor was mounted by concentric rubber seals into a flow cell.

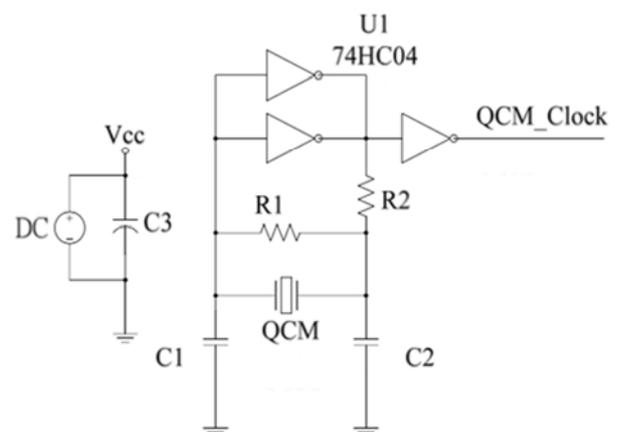


Figure 6. The circuit diagram of the Pierce oscillator [29].

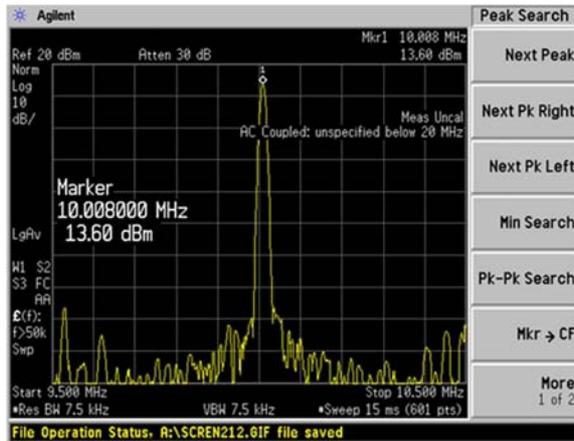


Figure 7. Output spectrum of the QCM oscillator in this work [29].

2.5. Procedures for Metal Ion Detection

Various concentrations of metal ion solutions were prepared by mixing in various ratios with the developed. During the detection, the developed and 300 μ l diluted metal ion solution were injected into the flow cell carefully with two syringe infusion pumps, respectively, at 0.01ml/min. After the frequency signal stabilized for several minutes, the QCM sensor generated a frequency-decrease after metal ions bounded with the function groups in the surface of sensing membrane. The frequency shifts in all experiments were calculated based on the average responses of the reactions with corresponding standard deviations of triplicate measurements.

3. Results and Discussion

3.1. Effect of pH on Response of the QCM Sensor

The effect of the pH of the solution on the response of the QCM sensor with a PVC based on copper(II) ionophore I (B)/ phosphate-modified dendrimer (A) volume ratio of 9 was studied by varying the pH in 1 μ M Cu (II) ion. The results are shown in Figure 8. The frequency shift of the QCM sensor increased with pH from 5 to 5.7, and decreased as the pH was increased further. A maximum frequency shift was observed in the pH 5.7. Therefore, the solution with pH 5.7 was used to study further the sensing properties.

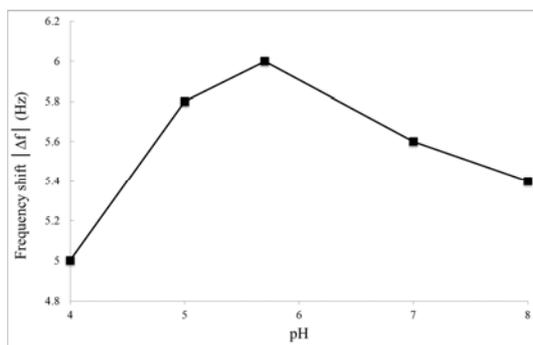


Figure 8. Effect of pH on the frequency shift of the QCM sensor in 1 μ M Cu(II) ion.

3.2. Effect of Volume Ratio of PVC Based Material on Copper(II) Ionophore I (B) to Phosphate-Modified Dendrimer (A) on Sensitivity and Selectivity of Cu(II) Detection

The performance of QCM sensors that were coated with sensing membrane with various volume ratios of B to A was studied and the results are shown in Table 1. Selective recognition of the target ions is an important characteristic of a QCM sensor. The selectivity factor is defined as the change in the ratio of the resonant frequency of the sensor in response to an interfering metal ion to that in response to a Cu(II) ion. The Zn(II) ion was selected as the competitor species because it has the same charge and a similar size. The thin film with a B/A volume ratio of 9 had higher selectivity than that with other ratios (Table 1). At a B/A volume ratio of 9, the prepared QCM sensor also exhibited high sensitivity for Cu(II) detection.

Figure 9 shows the selectivity to various metal ions of the sensing membrane with a B/A volume ratio of 9. The sensing membrane with a B/A volume ratio of 9 also exhibited high selectivity for Cu(II) in the presence of other metal ions. The high selectivity is believed to arise from the contribution of copper(II) ionophore I.

Table 1. Effect of volume ratio of B to A on performance of QCM sensor.

B/A	4/6	8/2	9/1
Sensitivity ^a (- Δ f, Hz)	4.2	7.2	17
Selectivity ^b	0.8	0.6	0.5

^a Sensitivity was defined as the frequency shift to 10 μ M Cu(II) ion.

^b Selectivity was defined as the change in the ratio of the resonant frequency of the sensor in response to Zn(II) ion to that in response to a Cu(II) ion at 10 μ M.

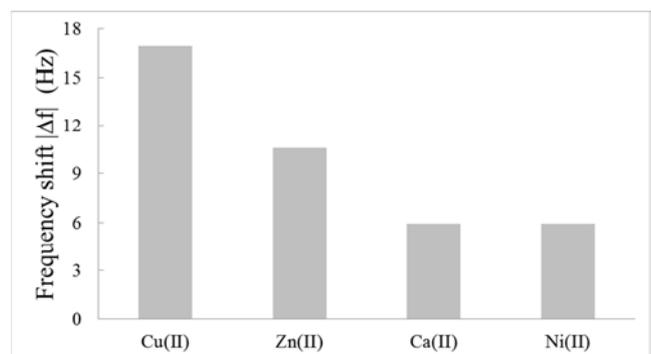


Figure 9. Selectivity of the QCM sensor with a B/A volume ratio of 9 to various metal ions at 10 μ M.

3.3. Characteristics of Metal Ion Detection

The sensing performance of the developed QCM sensor obtained by monitoring the frequency shift that was caused by the presence of Cu(II) ions. Each injection of Cu(II) solution, flowed over the surface of the developed QCM sensor, reduced the resonant frequency because the Cu(II) ions interacted with the sensing film binding sites. Then, the Cu(II) ions were washed away from the sensing film rapidly by dionized water, partially returning the resonant frequency

to its initial value. Therefore, this developed QCM sensor based on mixture of phosphate-modified dendrimer and ionophore exhibited partially reversible detection of the Cu(II) ion. Figure 10 plots the change in resonant frequency of the developed QCM sensor with a B/A volume ratio of 9 as a function of the concentration of Cu(II) ions. The sensitivity of the sensor to the Cu(II) ions concentration is roughly linear with $R^2 = 0.9025$ in a logarithmic coordinate system.

Table 2 lists the results of previous studies for detecting Cu(II) ions in solution [30, 31]. These QCM sensors developed in this study had also short response time that was about 40 seconds. This QCM sensor developed in this study provides a good candidate for the detection of Cu(II) ions.

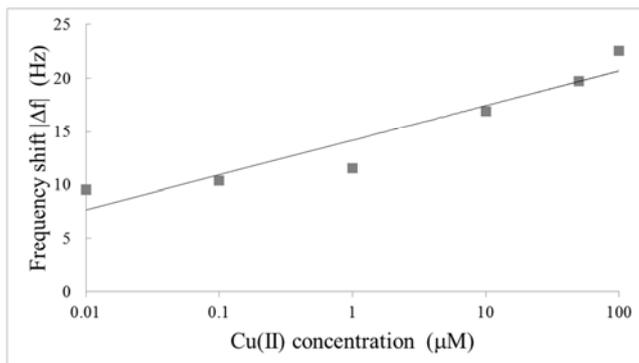


Figure 10. Dependence of change in resonant frequency of the QCM sensor, prepared with a B/A volume ratio of 9 on concentration of Cu(II) ions.

Table 2. Previous research for detecting Cu(II) ions in solution.

Sensor	Sensitivity	Linear range	Response time	Reference
MIP-based QCM	1.5 Hz/μM	0.001–50 μM	6 min	[30]
4-CP-SPEs	11 nA/M	0.0075–0.18 μM	-	[31]
This study	1.4 Hz/decade	0.01-100 μM	40 s	

4. Conclusion

In this study, a new sensing membrane of mixture of phosphate-modified dendrimer and ionophore has been synthesized. It has been applied for Cu(II) metal ion sensing by QCM sensor at room temperature. The linear sensing range of Cu(II) ion was from 0.01 μM to 100 μM. This developed QCM showed short response time that was about 40 seconds. The experimental results indicated that this developed QCM sensor based on combining phosphate-modified dendrimer and ionophore could be used for direct detection of Cu(II) metal ion with high sensitivity, good selectivity, satisfactorily good linearity, and fast response. Therefore, the QCM sensor developed in this study provided specificity with suitable for real-time detection of Cu(II) ions in environmental samples.

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