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Detection of Cu(II) Ion in Water Using a Quartz Crystal Microbalance

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Abstract: Drinking water from a tap is a source of potential exposure to environmental contaminants. This requires that public water supplies should be regularly monitored for heavy metals. Many of heavy metal ions are retained and accumulated in water strongly. Consequently it has entered the food chain to threaten human health. A quartz crystal microbalance (QCM) based on a phosphate-modified dendrimer film was investigated for direct detection of Cu(II) metal ion in water. This QCM sensor exhibited the high sensitivity and the short response time to Cu(II) metal ion.

Keywords: Crystal Microbalance, Dendrimer, Metal Ion, Sensitivity

1. Introduction

The chemical industry is highly diverse and a large number of chemical products are used and produced in manufacturing processes. It has resulted in the formation of wastewater contaminated with organic and inorganic substances of very different composition and volume [1-2]. Hence, heavy metals released by industrial activities are increasingly being found in freshwater to affect the quality of water bodies. Pollution caused by heavy metal ions is a long-term and irreversible process. Consequently it is a significant and emerging threat to public health. 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 [3]. 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 [4]. Its deficiency and excess lead to malfunction of the liver, heart diseases, neurological disorders, and deterioration of connective and bone tissues [1].

Most heavy metal ions in aqueous solution were measured using analytical instrumentation in laboratories such as atomic absorption spectroscopy [5], high performance liquid chromatography [6], and inductively coupled plasma-mass spectrometer [7]. These instrumentations are expensive and a well-trained operator is required. The advantages of a quartz crystal microbalance (QCM) are generally real-time, sensitive response and relatively inexpensive cost. A QCM oscillates at a specific frequency when an AC voltage is applied over its electrodes. The mass change per unit area at the QCM electrode surface relates to the observed change in oscillation frequency of the QCM, as shown by the Sauerbrey equation [8].

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

where Δf is the frequency change, f_o is the resonant frequency, Δm is the mass change, ρ_q is the density of quartz, μ_q is the shear modulus and A is Au electrode area. Frequency shifts of a QCM provide information on absorbed mass changes at QCM surface [9]. Therefore, the QCM was utilized in various fields such as environmental protection [10-12], lead acid batteries [13-16] and biomedicine [17-19].

For constructing functional and efficient chemical sensors, the modification of sensing films on the QCM electrode was been studied to greatly improve their properties [20]. Dendrimers are branched polymers with well-defined sizes and geometry [21-22]. Ability of dendrimers to coordinate metal ions in their interior branches or in the exterior units is developed the sensors with the selectivity and sensitivity of the analysis. These structural features endow them with the ability to encapsulate small guest molecules and act as nanocontainers for ions.

In this paper, a new design of sensor which combines high sensitivity of dendrimer with QCM detection 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. Preparation of Dendrimer Sensing Membrane

PAMAM dendrimer (ethylenediamine core, G5), whose chemical structure is shown in Figure 1, was dispersed in phosphorous acid solution with ultrasonic bath for 7 h and then rinsed by deionized water. In order to enhance the mechanical properties, the obtained phosphate-modified PAMAM dendrimer was mixed with 2.1wt% PVC in DMF solution.

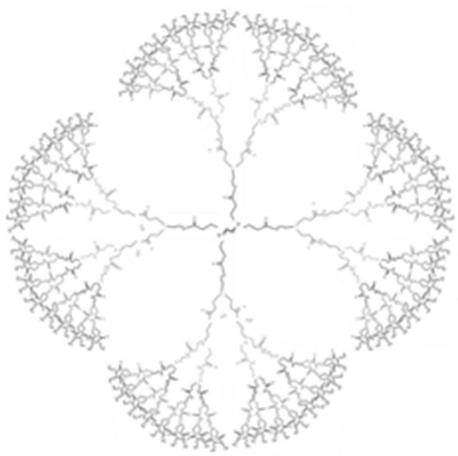

Figure 1. *Chemical structure of ethylenediamine core G5 PAMAM dendrimer.*

2.2. Fabrication of the QCM Sensor

The QCM device (Taitien Co., Ltd, Taiwan) with an operation frequency of 10 MHz was used in this work. The sensing membrane solution was dropped onto the electrode surface at room temperature. Then the samples were dried in the oven at 80°C. Finally, the samples were rinsed again with deionized water and dried with N_2 gas.

2.3. The QCM Experimental System

A QCM device based on the phosphate-modified dendrimer was coupled inside the flow cell (Figure 2), which was designed with a temperature controller shown in Figure 3 was maintained at 20°C, illustrated in Figure 4.

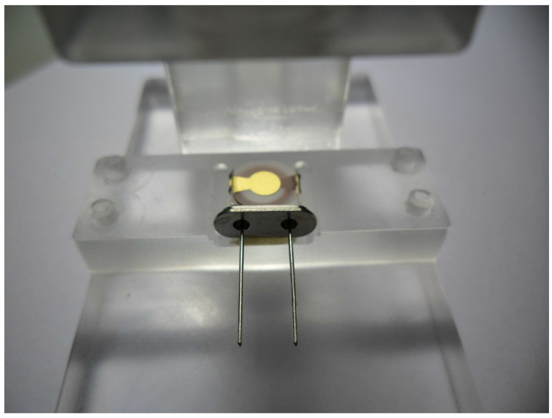

Figure 2. *A QCM device coupled inside the flow cell in this work.*

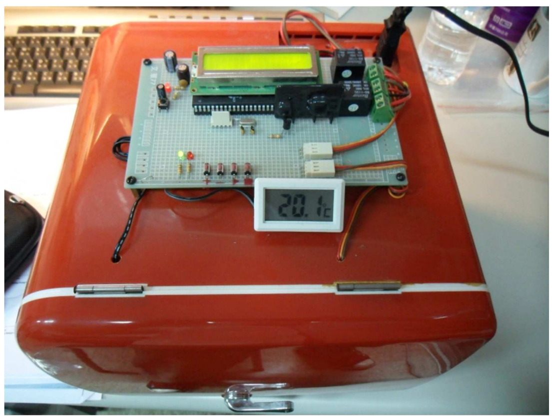

Figure 3. *The temperature controller used in this work.*

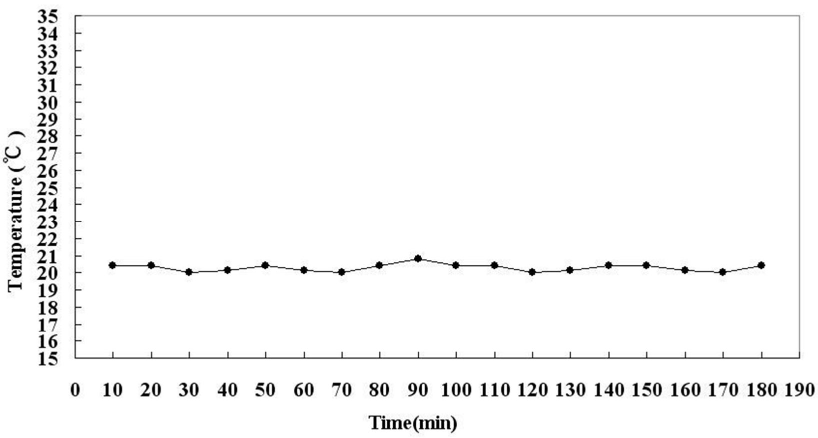

Figure 4. *Output of the temperature controller used in this work.*

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 [23]. The QCM experiences a large reduction in its quality factor that caused by the liquid. The Pierce oscillator design plotted in Figure 5 provides a great stability in frequency and a low phase noise, so the Pierce oscillator shown in Figure 6 was applied in this work to maintain the necessary loop gain and phase for the oscillation in a wide margin of values of the loss resistances of the QCM. Output spectrum of the QCM oscillator shown in Figure 7 indicates QCM generated stable oscillation occurred at 10 MHz.

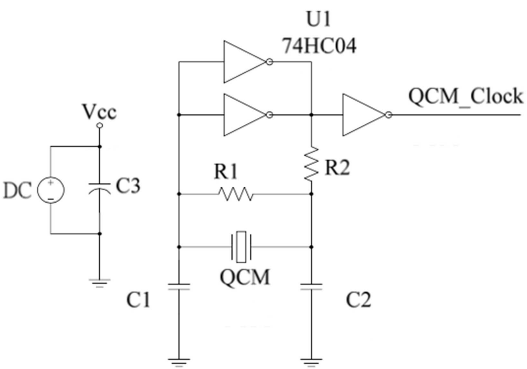

Figure 5. *The circuit diagram of the Pierce oscillator.*

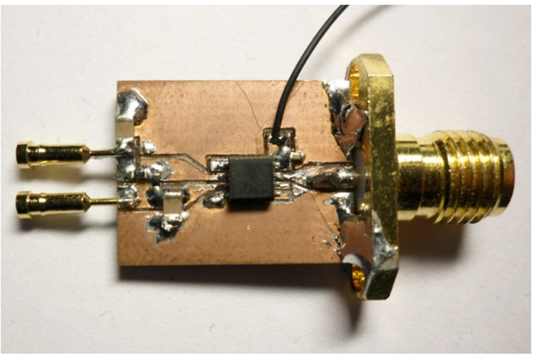

Figure 6. *A photograph of the Pierce oscillator used in this work.*

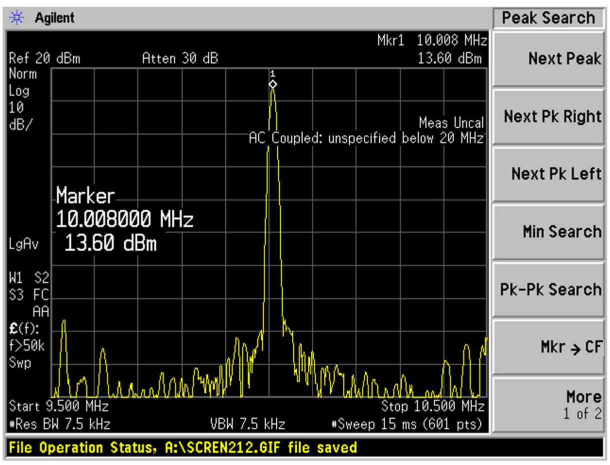

Figure 7. *Output spectrum of the QCM oscillator in this work.*

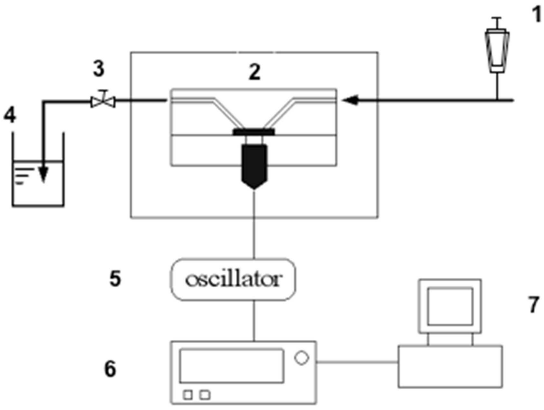

Figure 8. *QCM measurement system. 1: micro-injector; 2: flow cell; 3: valve; 4: waste; 5: oscillator circuit; 6: frequency counter; 7: computer.*

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). The QCM measurement system is illustrated in Figure 8.

2.4. Procedures for Metal Ion Detection

Various concentrations of metal ion solutions were prepared by mixing in various ratios with the deionized water. During the detection, 300 µl diluted metal ion solution were injected into the cell carefully with a micro-injector (KDS 200, KD Scientific, USA) at 0.01ml/min. After the frequency signal stabilized for several minutes, the QCM sensor generated a frequency-decrease after metal ions bounded with phosphorus groups in the surface of dendrimer. 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. Surface Morphology of the QCM Sensor

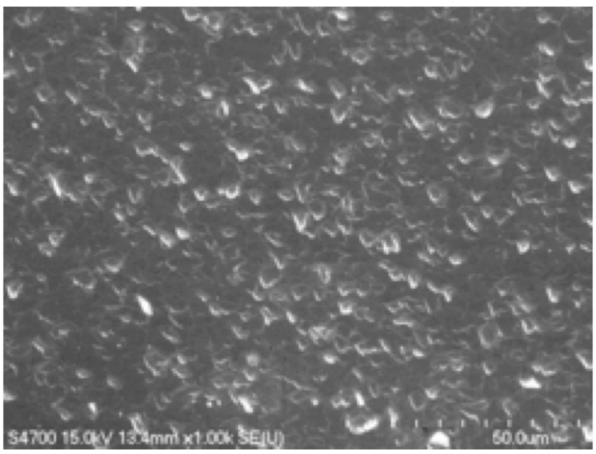

Figure 9. *SEM images of the phosphate-modified dendrimer modified crystal electrode.*

SEM was used to monitor and characterize the surface morphology of the QCM sensor after the modification process. Figure 9 shows that the surface morphology of the phosphorus-modified dendrimer modified Au crystal electrode has some small cell-like protrusions.

3.2. Effects of Fabrication Conditions of the QCM Sensor

The QCM sensor was fabricated with a drying step after the phosphate-modified dendrimer was deposited. The effect of drying time between 3 h and 5 h on metal ion detecting of the QCM sensor based on the phosphate-modified dendrimer with 2.1wt% PVC was shown in Figure 10. The frequency shift of the QCM sensor result from detecting 1 μM Cu(II) ions gradually increased with drying time from 3 h to 5 h. There are some small dark spots and lines were observed on the surface of these films at drying time of 5 h. Therefore, 4 h was selected as the optimal drying time in this study.

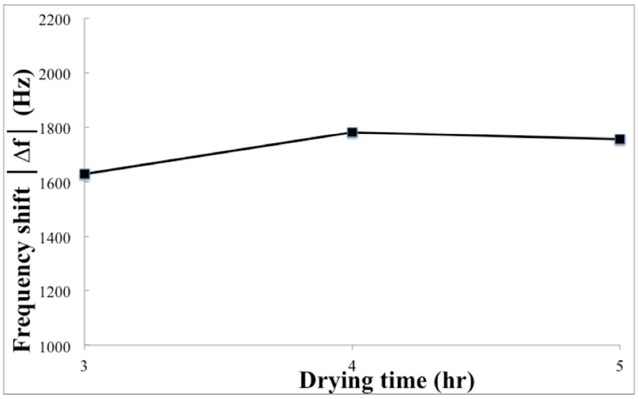

Figure 10. *Effect of drying time on frequency shift of the QCM sensor based on the phosphate-modified dendrimer with 2.1wt% PVC, measured at 0.01 μM Cu(II) ions in pH 5.7.*

3.3. Effect of pH Condition

It is known that the pH of a solution is important for metal trace detection. Figure 11 plots the effect of solution pH between 5 and 8 on the response of a QCM sensor based on the phosphate-modified dendrimer in 1 μM Cu(II) ions. The oscillation frequency of the QCM sensor increased with pH from 5 to 5.7, and decreased as the pH was increased further. Therefore, the solution with pH 5.7 was used in this study.

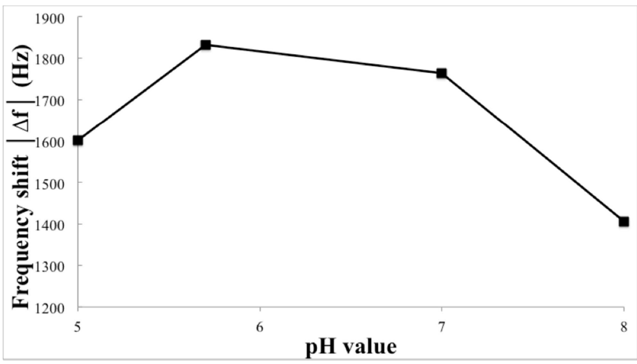

Figure 11. *Effect of pH on frequency shift of the QCM sensor based on the phosphate-modified dendrimer, measured at 1 μM Cu(II) ions.*

3.4. Characteristics of Metal Ion Detection

The results of detection curve of the QCM sensors based on the phosphate-modified dendrimer to various concentration of Cu(II) solution ranging from 0.0001 μM to 1 μM are plotted in Figure 12. An linear increased frequency shift was observed on the QCM sensor when increasing the Cu(II) ions concentration, revealing the absorption ability of the Cu(II) ions on the QCM sensor. Figure 13 shows the corresponding response time. The response time of the sensor was calculated as the time required to reach 90% of the saturation value upon exposure to Cu(II) ions. These QCM sensors had short response time that was less than 40 seconds.

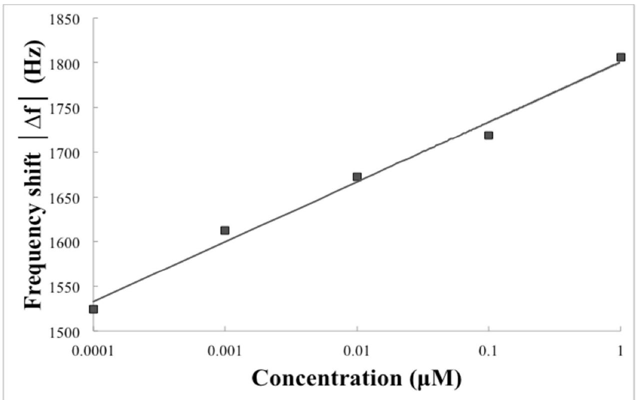

Figure 12. *The frequency shift of the QCM sensors based on the phosphate-modified dendrimer to 10^{-4} μM – 1 μM Cu(II) ions in solution.*

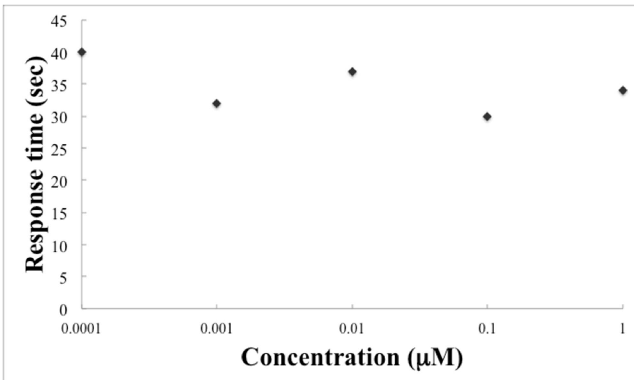

Figure 13. *Response time of the QCM sensor based on the phosphate-modified dendrimer at different Cu(II) ions in solution.*

4. Conclusion

In this study, a phosphate-modified dendrimer sensing membrane has been synthesized and characterized. 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 0.0001 μM to 1 μM. This developed QCM showed short response time that was less than 40 seconds. The experimental results indicated that the phosphate-modified dendrimer QCM sensor could be used for direct detection of Cu(II) metal ion with high sensitivity and fast response. We will develop this QCM sensor for detecting different metal cations, such as Ca(II), Mg(II), Zn(II), Co(II), Ni(II), Ag(I), and Fe(III), at room temperature in the future.

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