A PORTABLE MINIATURIZED PB^{2+} DETECTOR USING ION-RESPONSIVE HYDROGEL WITH WIRELESS INTERROGATION CAPABILITY

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ABSTRACT

This paper presents a passive wireless Pb^{2+} sensor by employing ion-responsive hydrogel with an inductor capacitor (L-C) resonator. When water passes through the device flowing into a hydrogel cavity, the hydrogel in the cavity swells and changes the capacitance of the integrated L-C resonator, which in turn changes the resonant frequency that can be remotely detected by using the phase-dip technique. The measured results show the proposed device gives 4.5% shifting of resonant frequency for a water sample with Pb^{2+}concentration 10^{-10} M, which is about two orders of magnitude smaller than the Pb^{2+} concentration harmful to human, which indicates the effectiveness of the proposed device.

INTRODUCTION

Developing simple and portable method for detecting trace analytes that are harmful to human health and environment is very desirable [1-3]. It is quite frequent that trace lead ions (Pb^{2+}) can be found in tap water supplied by old lead pipes. Therefore, methods to detect Pb^{2+} in water resource is essential to prevent harmful Pb^{2+} analyte from entering human body through drinking water.

Typical techniques for trace metal ion analysis require sophisticated techniques (e.g., mass spectroscopy [3,4], atomic absorption spectroscopy [6,7], potentiometric methods [8,9], optical methods [10-13] and so on), and require professional staff to carry out the procedures in laboratories. In recent years, specifically functionalized hydrogels were developed for various specified applications such as ion-recognition [14]. Zhang et al. [15] investigated the poly(*N*-isopropylacrylamide-*co*-benzo-18-crown-6-acrylamide) [P(NIPAM-*co*-B18C6Am)] ion-responsive characteristics and the ion–concentration dependence of the volume ratio with different contents of B18C6Am.

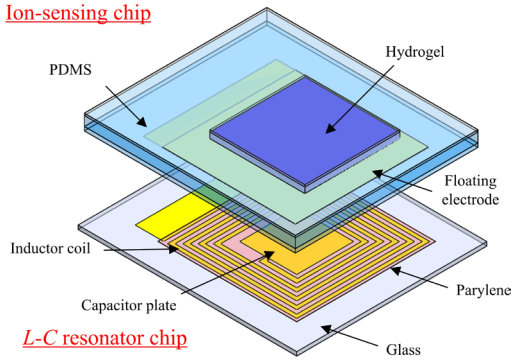
P(NIPAM-co-B18C6Am) have been proposed to detect Pb^{2+} trace due to its high sensitivity and good selectivity to trace Pb^{2+} ions [16]. S. Lin et al. [17] reported a sensing device using stimuli responsive hydrogel for real-time detection of trace Pb^{2+} analytes. Although the aforementioned technique has demonstrated great potential for accurate detection of trace Pb^{2+} ions, a portable sensor system with simple operation protocol has yet to be developed.

In this paper, we developed a highly sensitive portable miniaturized Pb^{2+} detector using ion-responsive hydrogel integrated with a passive inductor/capacitor (L-C) resonator [18]. The proposed device consists of a polydimethylsiloxzne (PDMS) ion-sensing chip and an L-C resonator chip. The PDMS ion-sensing chip can be used to sense the presence of Pb^{2+} ion, and the L-C resonator chip embedded with a capacitor plate and an inductor coil can be used to wirelessly retrieve the measurement result by the phase-dip technique using an external interrogation unit. The proposed device can be easily fabricated using a simple micromachining techniques, and the hydrogel material embedded in the device is easy to handle.

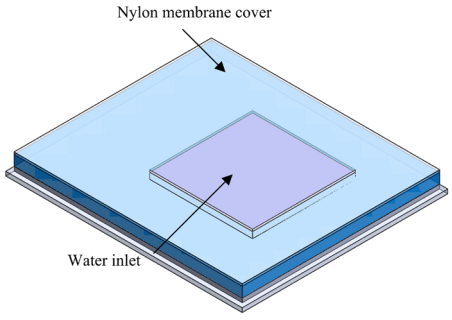
The major advantage of the proposed device is that the sensor unit does not require any onboard power and controller/driver circuitry for operation. Therefore, the devices are suitable for low-cost or portable applications. The proposed device is designed for the scenarios such as onsite detection of Pb^{2+} ions concentration in water supply source or in waste water. In this case, it is very desirable that the sensor is portable and does not need and circuitry and battery. In addition, wireless noncontact detection is very convenient for users when retrieving data.

DESIGN AND PRINCIPLE

Figure 1(a) shows the exploded view of the proposed hydrogel-based Pb^{2+} sensor. The proposed device consists of a PDMS ion-sensing chip and a L-C resonator chip. The PDMS ion-sensing chip comprises of a hydrogel reservoir containing an ion-responsive hydrogel and a nylon membrane filter covering the hydrogel reservoir. The L-C resonator chip is a glass substrate with a micromachined capacitor plate and an inductor coil. A parylene layer deposited on top of the glass substrate serves as the insulating layer between the two capacitor electrodes. Figure 1(b) shows the schematic of the assembled device.



(a)



(b)

Figure 1: (a) Exploded view of the hydrogel-based Pb^{2+} sensor. (b) Schematic of the proposed Pb^{2+} sensor.

For selectively recognizing trace Pb^{2+}, we use poly(N-isopropylacrylamide-*co*-benzo-18-crown-6-acrylamide) [P(NIPAM-*co*-B18C6Am)] hydrogel with NIPAM units as actuating material and B18C6Am units as ion signal sensing receptors. Figure 2 shows the curves which describes the temperature dependence of the volume for hydrogels with or without Pb^{2+} ions. Initially, the hydrogel shrinks in pure water at T_0, which is higher than the volume phase transition temperature (VPTT) of the hydrogel in pure water. After introducing trace Pb^{2+} in water, the B18C6Am units capture Pb^{2+} and form stable B18C6Am/Pb^{2+} host-guest complexes via molecular recognition. As a result, the curve of volume vs. temperature shifts due to the electrostatic repulsion among the charged B18C6Am/Pb^{2+} complex groups, and the corresponding VPTT shifts to $VPTT_{Pb}$. Therefore, the microgel isothermally swells to a certain degree depending on the Pb^{2+} concentration.

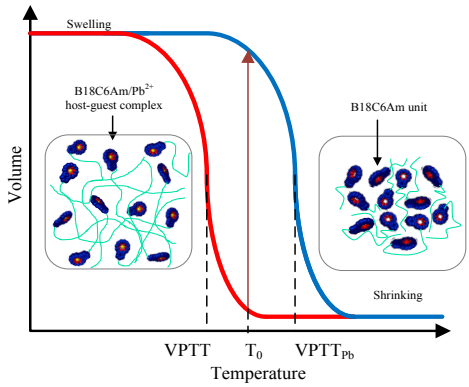


Figure 2: Schematic of the operation of ion-responsive hydrogel.

Figure 3 shows the operational principle of the proposed Pb^{2+} detector. Figure 3(a) is the cross-sectional view of the device before activation. Figure 3(b) shows that the formation of the B18C6Am/Pb^{2+} host-guest complexes gives rise to the swelling of the hydrogel. As a result, the hydrogel deforms the floating electrode of the capacitor in the integrated passive L-C resonator. Subsequently, the gap of the capacitor decreases and the capacitance increases, resulting in the shift of the resonant frequency of the L-C resonator.

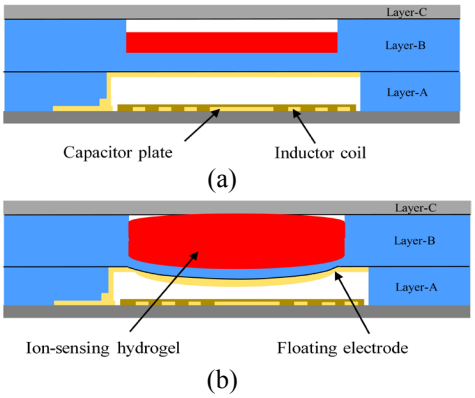


Figure 3: Schematic of the operation of proposed Pb2+ detector. (a) The cross-sectional view of the device. (b) The capacitance changed by hydrogel swelling.

FABRICATION

The PDMS ion-sensing chip comprises three layers: Layer-A, Layer-B, and Layer-C. The floating electrode of the capacitor is implemented on Layer-A. The hydrogel cavity is on Layer-B. Layer-C, which consists of a nylon membrane filter and a patterned PDMS film, is used to seal the cavities of Layer-II. Figure 4 shows the fabrication process for the proposed Pb^{2+} sensor. Figure 4(a) shows the process flow of the PDMS structure layers (Layer-A and Layer-B). Figure 4(b) shows the process flow of the glass substrate. Figure 4(c) shows schematic of the PDMS structure after filling ion-responsive hydrogel. The soft lithography technique was employed to fabricate the PDMS layers using with SU-8 molds. The preparation of PDMS polymer is as follows: the PDMS prepolymer and curing agent (Sylgard 184A and 184B, Dow Corning) were mixed at a 10:1 ratio. After stirring and degassing, the prepared PDMS mixture was poured onto the patterned SU-8 master (SU-8 2050, MicroChem). The cured PDMS layer was peeled from the master substrate after curing at 90° C for 60 min.

As show in Figure 4(a), metal films of chromium (Cr, 1000 Å) and gold (Au, 3000 Å) were deposited on Layer-A using an E-beam evaporator. The floating electrode was patterned by using a shadow mask during the deposition process. Layer-A and Layer-B were bonded together after oxygen plasma treatment. Figure 4(b) illustrates the lift-off process for patterning a Cr/Au (1000/3000 Å) layer on a glass substrate. The patterned metal film is then protected by a parylene layer (5 µm) which serves as the insulating layer between the electrodes of the capacitor. The bonded PDMS structure was also bonded with the glass substrate after using oxygen plasma treatment. The ion-sensing hydrogel was subsequently loaded in situ by polymerizing the pregel solution in the hydrogel cavity, as shown in Figure 4(c). As shown in Figure 4(d), Layer-C was fabricated by patterning PDMS on a nylon membrane filter. The patterned PDMS provides surfaces for bonding Layer-C onto Layer-B, and the membrane filter serves as the opening for sample solution to flow into the reservoir. The schematic of the assembled device is shown in Figure 4(e).

The *in situ* synthesis of the ion-sensing hydrogel is described as follows [15]: 2mL solution which contains 0.3 mmol monomer benzo-18-crown-6-acrylamide, 2.0 mmol monomer N-isopropylacrylamide, 0.042 mmol cross-linker N,N'-methylene-*bis*-acrylamide, and 0.036 mmol photoinitiator 2,2'-azbois(2-amidi-nopropane dihydrochloride) was prepared in a glass vial. Then the pregel solution was loaded in the hydrogel cavity using a micropipette, and then was irradiated with UV light (wavelength 365 nm) for 140s. Figure 5(a) is Layer-A with the floating electrode. The thickness of the layer is 200 µm. Figure 5(b) shows Layer-B with the hydrogel cavity whose dimension is 5500 µm x 5500 µm x 300 µm. Figure 5(c) shows the nylon membrane cap with patterned PDMS film. The thickness of the layer is 100 µm. Figure 5(d) shows the L-C resonator chip with the patterned capacitor electrode and the inductor coil. The gap between the electrodes of the capacitor is 20 µm. Figure 5(e) shows the picture of the assembled hydrogel-based Pb^{2+} sensor. The dimensions of

the device are 11.5 mm x 10 mm x 1.5 mm.

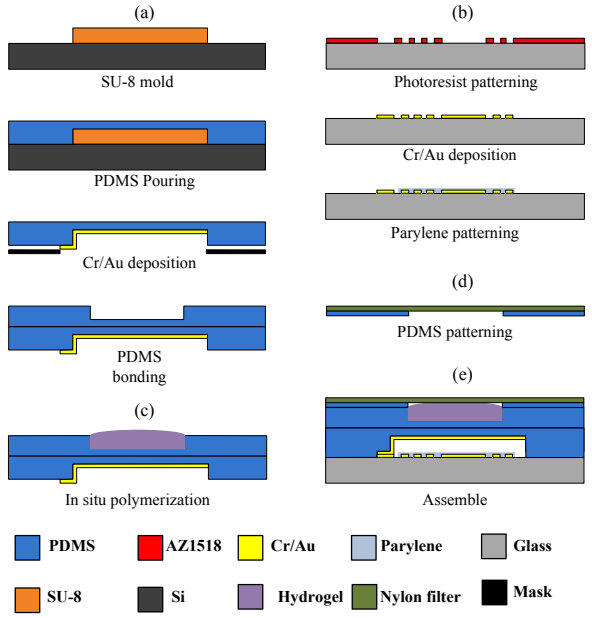


Figure 4: The fabrication processes of the proposed Pb2+ sensor.

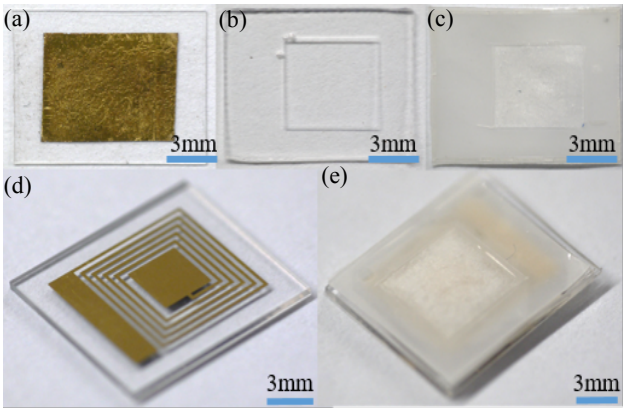


Figure 5: The fabricated components and assembled device. (a) The floating electrode. (b) Hydrogel cavity. (c) Nylon membrane cap. (d) The capacitor plate and the inductor coin. (e) The assembled hydrogel-based PB^{2+} sensor.

MEASUREMENT AND DISCUSSION

The experimental setup for remotely measuring the resonant frequency of the L-C resonator is showed in Figure6 (a). An impedance analyzer (HP4396A, Agilent) integrated with an RF impedance test adapter (43961A, Agilent) was employed to measure the impedance of the external coil that was coupled to the coil (inductor) of the L-C resonator embedded on the Pb^{2+} sensor. The diameter of the external coil is 4 mm.

A sample collecting cup was also realized by using a 3D printer, as shown in Figure 6(b). The proposed sensor chip is installed at the bottom of the cup. A draining hole is at the bottom of the cup and is originally plugged. 10ml sample solution was collected in the cup. After 20 min, the draining hole was unplugged, and the sample solution was drained out. Then, the collecting cup was placed above the external coil of the RF impedance test adapter to perform wireless interrogation, as shown in Figure 6(c).

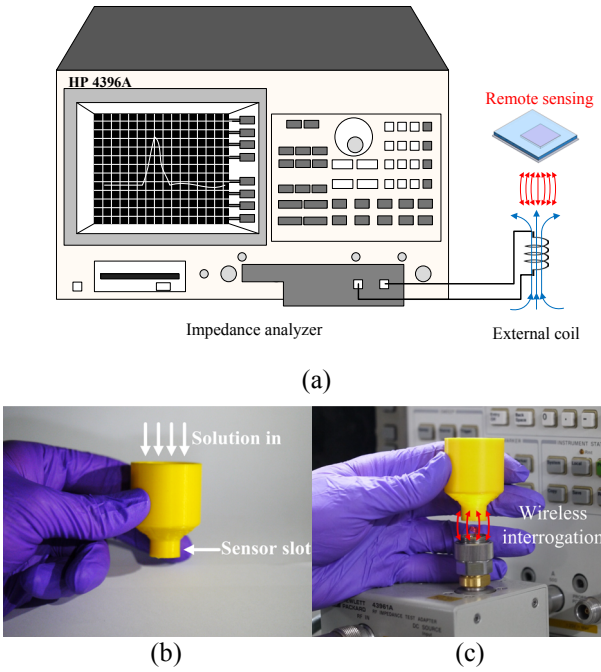


Figure 6: (a) The configuration for the phase-dip technique. (b) The portable test kit. (c) Setup for wireless interrogation.

Figure 7 shows the measured phase-dip phenomena of the external coil caused by inductively coupling with the proposed sensors. The dip in the measured phase curve coincides with the resonant frequency of the L-C resonator on the sensor.

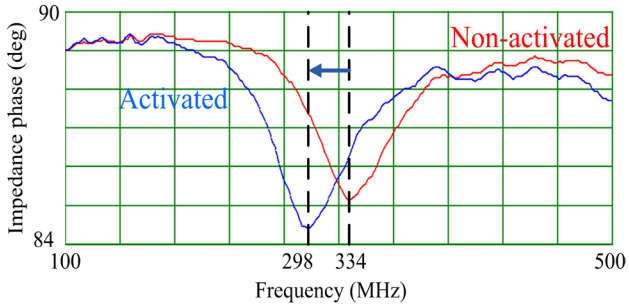


Figure 7: Phase-dip phenomena of the external coil antenna caused by inductive coupling with the proposed sensor.

Figure 8 shows the measurement of resonant frequency after switching the sensor from DI water to Pb^{2+} solution. Shifting in resonant frequency can be observed within 20 min for the solution with Pb^{2+} concentration ranging from 10^{-10} to 10^{-4} M. Note that 5% shift of resonant frequency can be detected for Pb^{2+} concentration ranging from 10^{-10} to 10^{-8} M, which is much lower than the guideline value of the World Health Organization for drinking water (4.83x10-8M), which indicates the proposed Pb^{2+} sensor has very high sensitivity.

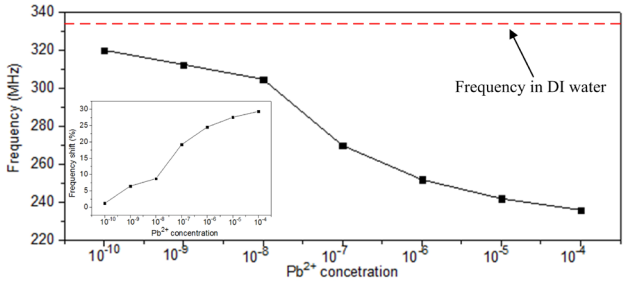


Figure 8: Measurement of resonate frequency after switching the sensor from DI water to Pb2+ solution.

CONCLUSION

This paper presents the development of an ion-responsive hydrogel based Pb^{2+} sensor. The proposed sensor employs P(NIPAM-*co*-B18C6Am) ion-responsive hydrogel for activation. The device consists of a passive inductor/capacitor (L-C) resonator chip monolithically integrated with a capacitor and an inductor coil, and a PDMS ion-sensing chip containing ion-responsive hydrogel. The hydrogel swells upon recognizing Pb^{2+} ions, and the capacitance of the integrated L-C resonator increases. The L-C resonator is used for transmitting the sensed signals wirelessly. The proposed sensor is of high sensitivity and rapid detection performance for real-time Pb^{2+} detection.

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