METAL ION DETECTION OF NOVEL CONJUGATED-POLYMER SENSOR FIBERS FABRICATED WITH 3-D HYDRODYNAMIC FOCUSING

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ABSTRACT
We propose a novel method to detect metal ions by using polydiacetylene (PDA)-embedded sensor microfibers fabricated with a 3-D hydrodynamic focusing technique. PDA, conjugated polymer, has a unique optical property to transform its color from visible blue to fluorescent red by metal ions. Previously we developed microfluidic PDA sensor systems by applying 2-D hydrodynamic focusing techniques. Now we use 3-D hydrodynamic focusing technique to fabricate PDA hydrogel microfibers to detect Al³⁺ and Zn²⁺ ions.

KEYWORDS: Microfluidic chip, 3D Hydrodynamic focusing, Sensor fibers, Polydiacetylene, Metal ion detection

INTRODUCTION
Polydiacetylene, a conjugated polymer, has a unique optical property to transform its color from visible blue to fluorescent red by certain metal ions as shown in Figure 1 [1, 2]. Due to its hydrophilic characteristic, PDA can be readily applied to a microfluidic chip to detect various stimulus [3-5].

It is often important to detect heavy metal ions from our environment because heavy metal ions can seriously damage to our organs or health. So far, the metal ion detection with bulk PDA is limited to about higher than 2 to 3mM of metal ions and consumes large amount of samples. To overcome the limits, we developed a novel method to fabricate PDA-embedded sensor microfibers by using 3-D hydrodynamic focusing technique on a microfluidic chip. This paper describes the diameter control of a sensor microfibers by varying flow rates and compares metal ion sensing capabilities of sensor microfibers of wet and dried phases.

Figure 1. Structure of PDA (A) and its color (top)/fluorescence (bottom) changes (B), and fluorescence spectral changes (C) upon stimulation. Transparent PDAs become blue when they are activated by 254 nm UV light. Then, they change their color and fluorescence to red upon stimulus.

EXPERIMENTAL SETUP
To fabricate PDA-embedded hydrogel microfibers, we mixed a diacetylene (DA) monomer solution with a sodium alginate solution (1.5 wt%) by 1:1 volume ratio. Then, the mixture was injected into the core channel of a microfluidic chip while a 780 mM CaCl₂ solution was inserted to the sheath channel as shown in Figure 2. A hydrogel microfiber with DA monomer is fabricated in the core flow of the microchannel. After collecting the hydrogel microfiber in a petri dish filled with DI water, the microfiber was exposed to 254 nm UV light to polymerize DA monomers. Finally, to evaluate the metal-ion-sensing capability of the PDA microfibers, droplets (~50μL) of 1mM Al³⁺, Ca²⁺, Cu²⁺, Fe²⁺, Hg²⁺, K⁺, Li⁺, Mg²⁺, Na⁺, Ni²⁺ and Zn²⁺ aqueous solutions were dropped on the fibers, and their fluorescence intensity changes were observed for 10 minutes.

Figure 2. Schematic of microfluidic chip. The chip was fabricated by using a capillary molding technique suggested by Lee’s group [6]. The inner and outer diameters of the capillary are 50 and 375 μm, and the main channel diameter is 670 μm.
To control the diameter of PDA fibers by varying the inlet flow rate, it was predicted theoretically using equation (1).

\[ R_s = R \left[ 1 - \left( \frac{Q_{\text{sheath}}}{Q_{\text{sheath}} + Q_{\text{core}}} \right)^{1/2} \right]^{1/2} \]

\[ R_s : \text{Fiber radius} \quad R : \text{Channel radius (670 μm)} \]

\[ Q : \text{Flow rate} \]

(1)

To detect metal ions on a microfluidic chip, we prepared two different kinds of PDA polymers by changing the head-group of the monomer molecules: PCDA-EDEA for Al\(^{3+}\) detection and PCDA for Zn\(^{2+}\) as shown in Figure 3.

![Figure 3. Molecular structure of DA monomers: PCDA-EDEA (A) and PCDA (B).](image)

RESULTS AND DISCUSSION

Figure 4 displays the color and fluorescence changes of wet and dried microfibers fabricated with PCDA-EDEA. It is evident from the fiber colors that both fibers successfully contain PDA sensor vesicles. The dried fiber appears more saturated in the blue color and fluorescence intensity than the other, probably due to the volume shrinkage. The diameters of the wet and dried microfibers are about 115 and 80 μm, approximately. Unlike PDA nanofibers fabricated by electrospinning [7], the PDA microfibers are easy to handle as exhibited in Figure 5. PDA microfibers fabricated with PCDA show almost same properties as these results.

![Figure 4. Optical and fluorescence images of wet (A) and dried (B) fibers before (upper row) and after (lower row) stimulation of 10mM α-Cyclodextrine solution.](image)

![Figure 5. Images of PDA sensor fibers handled by needles.](image)

By carefully varying the core and sheath flow rates of 3-D hydrodynamic focusing, we were able to control the diameter of PDA embedded microfiber. As shown in Figure 6, the fiber diameters are in excellent agreement with theoretical predictions.

![Figure 6. Fiber diameter changes with respect to the core flow rate (A) and the sheath flow rate (B).](image)

Finally, we evaluated the metal-ion-sensing capability of the PDA sensor microfibers of a wet phase. Figure 7 shows that the fluorescence intensity of fibers increases dramatically for the first 1 min when they are exposed to 1mM metal ions, and the fluorescence of PCDA-EDEA and PCDA fibers is strongest when they are exposed to Al\(^{3+}\) and Zn\(^{2+}\), re-
respectively. Additional experiments are underway with metal ions of lower concentrations and dried PDA fibers which are more convenient to handle and have better sensitivity than the wet ones.

Figure 7. Fluorescence intensity variation of wet PDA fibers with respect to time: Al$^{3+}$ detection with PCDA-EDEA (A), Zn$^{2+}$ detection with PCDA (B), and fluorescence images for Al$^{3+}$ detection (C).

CONCLUSION

We proposed a new method to detect metal ion using PDA embedded hydrogel microfibers fabricated using a microfluidic chip. Using 3-D hydrodynamic focusing technique and controlling flow rates, we were able to fabricate PDA embedded hydrogel microfibers with various diameters. Fabricated PDA sensor microfibers are then activated to blue phase by 254nm UV light. When the PDA sensor microfibers are exposed to metal ion solutions, fluorescence intensity of PDA sensor microfibers increases dramatically for the first 1min and is the strongest when PCDA-EDEA microfiber is exposed to Al$^{3+}$ ions and PCDA microfiber to Zn$^{2+}$ ions. Using PDA sensor microfibers, we were able to detect a lower concentration of metal ions than using bulk PDA solution. This indicates that certain metal ions can be detected by measuring the fluorescence intensities of PDA sensor microfibers. We expect that we can also detect other metal ions by employing structurally diverse diacetylene monomers into microfibers.

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REFERENCES


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