

PDMS マイクロ流路を用いた電気化学計測と可視・赤外分光法の融合的アプローチ  
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Development of PDMS microfluidic devices feasible for on-chip electrochemistry  
with visible and IR spectroscopy

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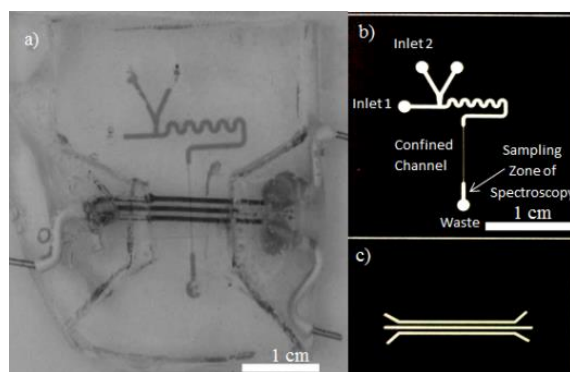
**[Introduction]** Microfluidic technique is a promising method for characterizing chemical and biological reactions with low sample consumption. Polydimethylsiloxane (PDMS) is transparent under visible light and is a soft material, which widely used for making microfluidic devices feasible for various kinds of experimental techniques. One of the authors published a paper applying FTIR microspectroscopy with a PDMS microfluidic device as a collaborative work with Dr. M. Srisa-Art in Chulalongkorn University, Thailand [1]. In addition, the other research group has developed a droplet-based microfluidics coupled with amperometric detection using chip-based carbon paste electrodes (CPEs) [2]. These researches provided a silver lining for the combination of optical and electrochemical approach in microfluidic device using PDMS as a useful material. We, therefore, planned to combine electrochemical experiment with visible and infrared spectroscopies on a microfluidic chip. Here, we demonstrated visible spectroscopy of electrochemical reactions of silicotungstic acid ( $\text{H}_4[\text{W}_{12}\text{SiO}_{40}]$ ), and infrared spectroscopy of electrochemical reactions of ferrocyanide ( $[\text{Fe}(\text{CN})_6]^{4-}$ ) as a test case.

**[Materials & Methods]** To fabricate microfluidics devices, T-junction is commonly used for droplet generation pattern. In this work, soft lithography was used as a traditional method for microchip fabrication. Briefly, T-junction microchannel was designed by AutoCAD then printed out as negative film, as shown in Figure 1 (b). After that SU-8, a well-known photoresist polymer, was used for microchannel-pattern fabrication on silicon-wafer.

To fabricate microfluidic devices for visible spectroscopy, PDMS was poured onto the master and left into 65 °C oven for 1 hour, and then peeled out from a master as microchannel of T-junction pattern appears.

Furthermore, a master of electrodes was fabricated using the method as well as using for T-junction's master. To fabricate electrodes, carbon paste which is a mixture of graphite powder, nujol oil, and PDMS (2:1:1, w/w) was filled into pattern channels and clean up with scotch tape Magic™, as illustrated in Figure 1 (c). In order to assemble a microfluidic device, the microchannel plate was undergone into the oxygen plasma and then bonded with the electrode plate immediately. Finally, electric wires were attached onto each electrode using silver paint as a binder, and then covered with epoxy glue for reducing noise and extending life time, as illustrated in Figure 1 (a).

For FTIR microspectroscopy, a spin coater was used to develop a thin PDMS film as



**Figure 1** (a) a complete microfluidic device with electric wires (b) microfluidic pattern on negative film with confine channel for droplet extension during pass CPEs (c) Electrode pattern on negative film

reported in the previous paper [1]. The thinner PDMS film was achieved by boned a supporting PDMS plate (5 mm thickness) upon a thin PDMS film (80  $\mu\text{m}$  thickness). This approach successfully prevented a rolling up and laceration of the PDMS sheet. After that, both PDMS films were boned using plasma bonding, and attached electric wires using a method as mentioned above.

To deliver fluid to microchannel, solution was filled into a 1 mL plastic syringe which connected with Teflon tubing and placed onto a syringe pump. Then, the solution was delivered through the tubing connecting to the reservoir at microfluidic channel with infusion mode of syringe pump. For visible detection, the microfluidic device was placed onto a clamp between a light source and a detector. The detection window was set at the end of confined channel. For the IR measurement, the microfluidic device was placed under IR-microscope. The experiment was done through the observation window with rectangular shape (5 mm x 5 mm). Subsequently, electric wires were connected to a potentiostat as working, counter, and reference electrodes, respectively, for both experiments.

Silicotungstic acid and potassium ferrocyanide purchased from Wako Pure Chemical Industries, Ltd. were dissolved in milliQ water at 0.1-0.5 M and in 0.1 M PBS pH 7.4, respectively. Cyclic voltammetry and amperometry were successfully employed in this work as an electrochemical method for electrochemical behavior and reaction studies, respectively. All electrochemical experiments were performed using a potentiostat (ER461, eDAQ).

**[Results]** For high-throughput study, droplets were formed by flowing oil (which is a 10:2 (v/v) mixture of perfluorodecalin and 1H, 1H, 2H, 2H-perfluoro-1-octanol), and aqueous solutions into the T-junction as done in the previous report [2]. Visible spectroscopy on electrochemical reduction of silicotungstic acid in droplets, using amperometric approach with -0.8 V applied potential, showed broad visible absorption spectrum in the whole observation range (400-800 nm). This result corresponds to color change of silicotungstic acid from colorless ( $\text{H}_4[\text{W}_{12}\text{SiO}_{40}]$ ) to blue ( $\text{H}_5[\text{W}_{12}\text{SiO}_{40}]$ ) and dark blue ( $\text{H}_6[\text{W}_{12}\text{SiO}_{40}]$ ) solution. The reductions were also confirmed by cyclic voltammograms.

On the other hand, infrared spectroscopy was performed on static condition. First, the microfluidic channel was filled with 0.1 M potassium ferrocyanide solution. Then, the electrochemical reaction was started by applying constant voltage which took place on the working electrode. The applied potential for amperometric method was followed electrochemical behavior from cyclic voltammogram which used from 0 to 0.5 V by fixing each potential for each experiment. After finishing the reaction, the solution was flushed by introducing a same solution using a syringe pump for the next reaction. Consequently, the  $\text{C}\equiv\text{N}$  stretching band for ferrocyanide was observed at  $2038\text{ cm}^{-1}$  and decreased its intensity in accordance with increase of the applied potential. Concomitantly, the  $\text{C}\equiv\text{N}$  stretching band for ferricyanide appeared at  $2115\text{ cm}^{-1}$ . The spectral change was more evidently observed between the working and reference electrode, not between the reference and counter electrode. Results indicated electron transfer process of electro- and IR-active species could be observed even through a microchannel which provided a great promise for diminishing of sample consumption as nanoliter scale in spectroelectrochemical approach in further study in near future.

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#### **[References]**

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