

# **Report on Visit to MESA+ Institute for Nanotechnology of University of Twente by International Training Program**

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This report describes the research activity during long-term research program in the International Training Program of young researchers sponsored by Japan Society for the Promotion of Science.

I visited to Twente University of Twente MESA+ Institute for Nanotechnology in the Netherlands from October 12 to December 10, 2010 by the program for incubating young researchers on plasma nanotechnology materials and device processing conducted by Plasma Nanotechnology Research Center in Nagoya University. Here, I report on the research environment, the research activities of Ph. D. students, and my research progress in MESA+ Institute for Nanotechnology.

### **1. The research environment and the research activities of Ph. D. students in MESA+ Institute for Nanotechnology**

MESA+ Institute for Nanotechnology, which is located in University of Twente, the Netherlands, is one of the most important institutes for nanotechnology all over the world. This institute is one of central institutes which leads NanoNed, the national project for nanotechnology in the Netherlands, and has the huge infrastructure for research of material and fabrication technology. This institute consists of 19 groups of various fields, such as physics, electrical engineering, chemistry and mathematics. Activating the collaborative research between each group, this institute aspires to achievement of breakthrough in the nanotechnology.

I engaged in the research activity in BIOS group directed by Prof. van den Berg. This group research mainly aims to contribute to the improvement of the quality of life by combining the micro- and nanotechnology with chemistry, physics and life science, using the microfluidic device called Lab-on-a-Chip.

BIOS group has around 50 members; Prof. van den Berg and other 6 scientific staffs, 5 technical staffs, 8 postdoctoral

fellows (Postdocs), 16 Ph.D. students, 7 master students and so on. Each scientific staff directs his/her own research projects with several Postdocs and Ph. D. students.

Ph. D. students seem the most active players in this group. Not only the number but also the mentality of Ph. D. students seems different from that of Ph. D. students in Japan. The system of doctoral course in the Netherlands is far different from that in Japan. Each scientific staff selects Ph. D. students in their group strictly. The scientific staffs evaluate the candidates not only in their research ability but also their character, communication ability and so on.

Ph. D. students usually begin their research at 9 a.m. and finish it at 6 p.m. (and leave the institute immediately). This style is far different from that in Japanese laboratories. They seemed to be very good at switching on and off. Once I asked a Ph.D. student why he went home so early. He replied that he wants to study the subjects which are not directly related to his research in his private time. He also said that he did all the effort to finish the daily experiments before 6 p.m. in order not to disturb his private study. These were impressive for me. In addition, scientific staffs expect a lot of Ph.D. students and discussed with them very frankly.

### **2. Research progress**

In this program, I developed the electrochemical measurement method for oil / water interfaces in microchemical chips with supervision of Prof. Eijkel in BIOS group. In the following part, details of this research are described.

#### **Introduction**

Emulsion, which means water-in-oil (W/O) or oil-in-water (O/W) micro- or nano- droplets, is one of the most important materials in our life. It is used in many industries such as cosmetics and food industry. Conventionally, emulsions are produced by strong mixing of immiscible liquids and the surfactant using a mixer.

However, it is difficult for this conventional method to produce monodispersed droplets and to control the size of droplets. In addition, It is also difficult to made W/O or O/W droplets selectively.

Recently, the techniques to generate microdroplets using microchemical chips are paid much attention (Fig. 1A and B). The mechanism of generating microdroplets in the microchemical chips is far different from that in the conventional method. As illustrated in Fig. 1C, dispersed phase (blue) is sheared by continuous phase (white). In this method, it is easy to control the size of microdroplets by changing flow rates of the continuous phase and/or the design of the microchannels. Furthermore, W/O or O/W droplets can be produced selectively with wettability control of the microchannel wall.

As described above, the microchemical chip can achieve precise control of the microdroplet production process. As an application, rapid extraction microchemical chip using the microdroplets was reported. Other applications, such as encapsulation of single cell in each microdroplet for biochemical analysis and screening estimation of chemical synthesis inside the microdroplets were also reported.

The high applicability the microdroplets enhances the importance of the microfluidic techniques. Therefore, mechanism of the microdroplet generation was investigated by many groups. However, there are a few methods for analyzing this phenomenon because droplets are generated within very short term ( $< 1$  ms) from very tiny W/O interface (several hundred  $\mu\text{m}^2$ ). Most researches are based only on hydrodynamic approach using a high speed camera. However, there remain a lot of unknown phenomena in the generation process. In order to clarify the generation process, not only the hydrodynamic approaches but also the physicochemical approaches, such as the observation of the absorption behavior of the surfactant (Fig. 1D), are required.

The objective of my research is to investigate an electrochemical measurement technique for analyzing surfactant behaviors during the microdroplet generation process. Much physicochemical information is expected from this measurement method.

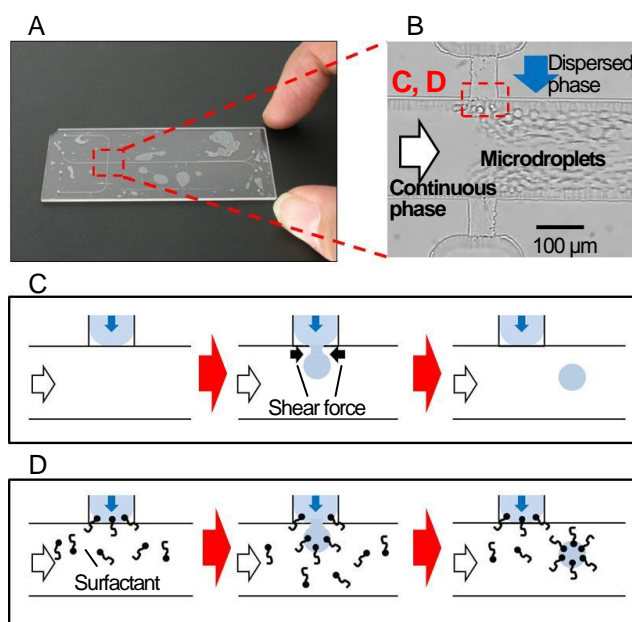


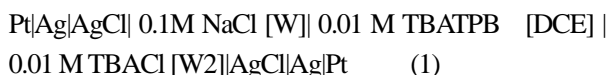
Fig. 1. The generation of microdroplets in microchemical chip. A) Microchemical chip. B) Micrograph of the microdroplet generation in the microchannel. C) Illustration of dispersed phase shearing by continuous phase. D) Illustration of surfactant behaviors during the generation.

In this program, the electrochemical measurement system for the liquid-liquid interfaces in the microchemical chip has been constructed and estimated. The voltammetry for the ion transfer at the interface of two immiscible electrolyte solutions (VITIES) was applied for the measurement in microchemical chips.

#### Measurement of VITIES in millimeter scale

Before measuring VITIES in a microchemical chip, the ion transfer at millimeter-sized interfaces was investigated. In this measurement, 1,2-dichloroethane (DCE) was used for the oil phase. Pt wire ( $\varphi = 200 \mu\text{m}$ ) covered by Ag|AgCl ink was used for working and counter/reference electrodes. As the supporting electrolyte, NaCl and tetrabutylammonium tetrphenylborate (TBATPB) were dissolved in the water and oil phases, respectively. The water phase contacted to the Pt|Ag|AgCl was used as the counter/reference electrode for oil phase few solid electrode works stably in the oil phase. The Ag|AgCl electrode was put in tetrabutylammonium chloride (TBACl) aqueous solution connected to the oil phase. As a result, the TBA ion selective electrode was prepared. Then, potential difference was applied to the two electrodes. By using this connection, potential and current

between the target W|O interface (droplet-generating interface) can be discussed. The voltammogram at the W|O was measured by scanning the potential difference from -0.2V to 0.6V and by recording the current between W and O.



The VITIES was measured using the cell illustrated in Fig.2. A small beaker was filled with oil phase (Fig. 2C). Ag|AgCl electrodes were placed in the glass cells having holes ( $\phi=2$  mm) at the bottom, and the cells were filled with each aqueous solution. The cells were introduced to the oil phase, and the interfaces for the measurement and the reference were generated (Fig. 2A and B).

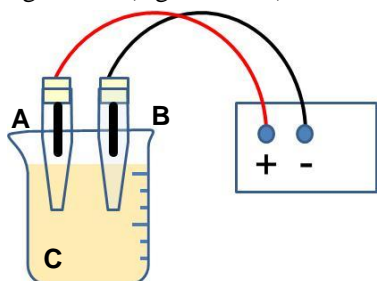


Fig.2. The measurement equipment for VITIES in millimeter scale. A) The Ag|AgCl electrode placed in NaCl solution (working electrode), B) The Ag|AgCl electrode placed in TBACl solution (counter/reference electrode), C) DCE containing TBATPB.

The voltammogram at W|O was obtained as Fig.3 (left). The positive current appearing over 0.4 V indicates the transfer of cation/anion from oil/water phase to water/oil phase (Fig.3 (right) A). In other word, this current flows when TBA ion transfers from DCE to water or Cl ion transfers from water to DCE. After that, the peak of negative current appeared at 0.3 V indicates the return of the TBA/Cl to DCE/water. In the same manner, the peak of negative current appeared under 0V is attributed to the TPB ion transfers from DCE to water or Na ion transfers from water to DCE. The peak of the positive current appeared during the scanning in positive direction indicates the return of the TPB/Na to DCE/water. As a result, measurement of ion transfer between W|O interface in millimeter scale was achieved.

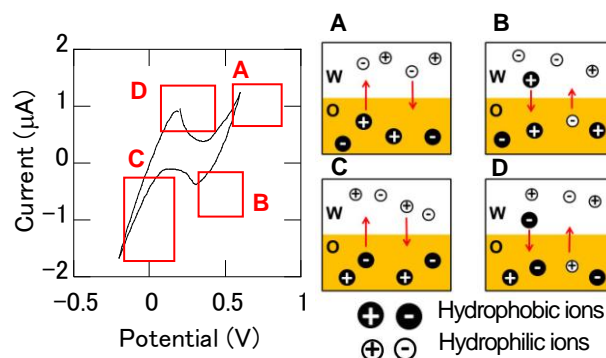
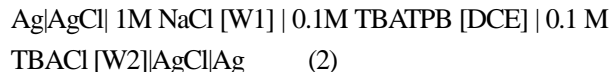


Fig.3. The voltammogram of ion transfer between W|O interface (left) and the explanations for each peak (right)

### VITIES measurement at the static W|O interface in microchemical chip

The VITIES measurement method in a microchemical chip was investigated. In order to reduce the solution resistance in the microchannels, much concentrated supporting electrolyte was used. Since the former Pt|Ag|AgCl electrode has less organic-solvent tolerance, new Ag|AgCl electrodes were prepared by electrodeposition of AgCl on Ag wire ( $\phi = 200 \mu\text{m}$ ).



In order to realize the configuration described in Eq.2, the glass microchemical chip was fabricated using a 2-step photolithographic wet-etching method (Fig. 4A). The width and depth of the shallow channel for generating microdroplets were  $70 \mu\text{m}$  and  $2 \mu\text{m}$ , respectively. The widths and depths of the other channels were  $220 \mu\text{m}$  and  $40 \mu\text{m}$ , respectively. The connectors for introducing liquids to the glass microchemical chip, were glued to the inlet-points, which is also used for connecting the electrodes to the microchemical chip (Fig.4B). The oil and water phases were introduced to the microchemical chip from the inlets L1 and L2, respectively. The distances between the electrodes and the interface were set to 6 mm. Here, the water phase for the counter/reference of the oil phase was put to the connector at the inlet E1. Thus, the interface at the junction of two microchannels was measured (Fig.4C).

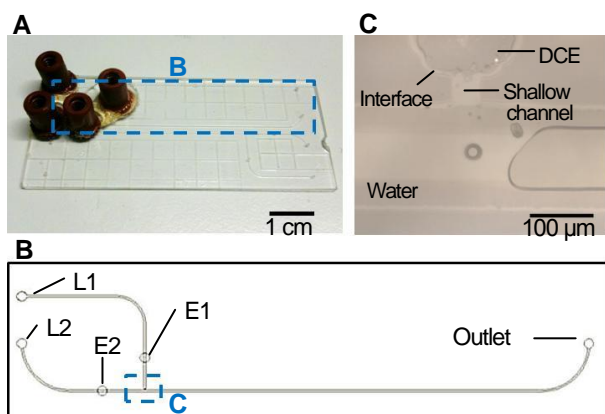


Fig.4. The microchemical chip for electrochemical measurement. A) The microchemical chip, B) Design of the microchannel (L1 and L2 are the inlets for liquids and E1 and E2 are the inlets for electrodes, C) the structure for microdroplet generation (width and depth of shallow channel are 70  $\mu\text{m}$  and 2  $\mu\text{m}$ , and the widths and depths of other channels are 220  $\mu\text{m}$  and 40  $\mu\text{m}$ , respectively).

At first, the linear-shaped voltammogram was obtained (Fig 5 (left)). The absence of polarized plateau region indicated that the ion transfer between the two phases was hindered. One possible explanation is that the counter/reference electrode did not work as designed.

With hydrophilic microchannel surface, the aqueous phase covers the surface and thin water film may be generated between the oil phase and the glass channel wall. Here we assumed that the two aqueous phases are connected with the thin film and high resistivity of the water thin film was measured in the voltammogram. .

In order to solve this problem, the channel was modified with hydrophobic octadecyltrichlorosilane. As a result, the voltammogram reflected the ion transfer through the interface was obtained.

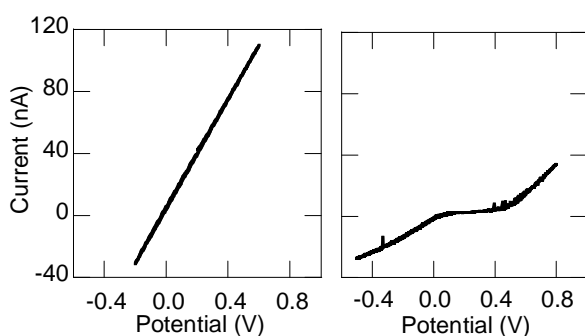


Fig.5. Voltammogram at the interface in microchemical chip. Left) measured in hydrophilic channel, right) measured in hydrophobic channel

Thus, the electrochemical measuring technique for static interfaces in the microchemical chip was established. This technique will be applied to measurements of the W/O interface during the droplet generation. Moreover, by measuring the interface in the presence of the surfactant, the mechanism of the microdroplet generation will be elucidated.

In this program, I learnt not only technical know-how, but also communication skill in English. During my stay in the Netherlands, I had some opportunities of discussion with Prof. Eijkel for several hours. In the beginning period, I slightly hesitated to speak English, but I became more confident in discussing scientific contents in English each time. This confidence enabled me to communicate with many people in English in not only about science but also in various occasions.

In addition, it was very exciting for me to meet different philosophies, cultures and arts of various countries. Now, I convince that the program gave me very good opportunity to think about my research itself and research carrier. Finally, I acknowledge Prof. Toyoda, Prof. Baba, Dr. Kaji, and those who gave me this precious opportunity in Nagoya University. I really appreciate Prof. van den Berg, Prof. Eijkel Dr. ir. Le Gac, and those who support my research activity in University of Twente. I also appreciate Prof. Yoshida of Kyoto Institute of Technology, who taught me the basic of electrochemical measurement.