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RESEARCH PAPER

Surface modification of a glass microchannel for the formation of multiple emulsion droplets

Hirotada Hirama[1] · Satoshi Wada[2] · Jiro Shimamura[2] · Yusuke Komazaki[2] · Tomoya Inoue[1] · Toru Torii[2]

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Abstract We herein report a method for the preparation of a glass microchannel capable of forming multiple emulsion droplets (i.e., water-in-oil-in-water and oil-in-water-in-oil) by locally controlling the wettability of the glass microchannel. Production of multiple emulsion droplets using a glass microchannel requires partial control of its wettability using a method that consists of two steps: (1) hydrophobization of a whole glass microchannel by filling the microchannel with octadecyltrichlorosilane (OTS) solution, and (2) local hydrophilization of the OTS-treated glass microchannel by exposure to ultraviolet light through a mask. However, conditions for the preparation of OTS-SAMs for controlling microchannel wettability and subsequent multiple emulsion droplet formation have not yet been reported. In this study, we investigated the conditions required to form multiple emulsion droplets and demonstrated formation of multiple emulsion droplets using a treated glass microchannel with multiple junctions. The glass microchannel prepared according to this method was able to form various aqueous and organic droplets due to its resistance to swelling.

Keywords Droplet microfluidics · Wettability control · Trichlorosilane · Multichannels · Self-assembled monolayer

1 Introduction

Handling of liquids in a microchannel requires the control of different surface properties depending on the intended use of the microchannel (Atencia and Beebe 2005). Among these surface properties, microchannel wettability (i.e., hydrophilicity and hydrophobicity) is an important property for the stable formation of a droplet. Specifically, a hydrophobic microchannel is required for the formation of an aqueous droplet [a water-in-oil (W/O) emulsion droplet], while a hydrophilic microchannel is required for the formation of an organic droplet [an oil-in-water (O/W) emulsion droplet]. Furthermore, both hydrophilic and hydrophobic properties are required in a microchannel for the formation of multiple emulsion droplets such as water-in-oil-in-water (W/O/W) and oil-in-water-in-oil (O/W/O) emulsion droplets.

Monodispersed W/O/W and O/W/O emulsion droplets can be produced using a wettability-controlled microchannel composed of either polydimethylsiloxane (PDMS) or glass (Abate et al. 2010; Barbier et al. 2006; Hwang et al. 2012; Seo et al. 2007; Utada et al. 2005). PDMS microchannels allow rapid prototyping of microchannels, and therefore, they are widely used, and various PDMS wettability control methods have been developed for the formation of W/O/W and O/W/O emulsion droplets (Abate et al. 2010; Barbier et al. 2006; Bauer et al. 2010; Hwang et al. 2012; Kim et al. 2015; Seo et al. 2007). The conventional methods, including layer-by-layer deposition of polyelectrolytes (Bauer et al. 2010),

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✉ Hirotada Hirama
h.hirama@aist.go.jp

[1] Research Center for Ubiquitous MEMS and Micro Engineering, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8564, Japan

[2] Department of Human and Engineered Environmental Studies, Graduate School of Frontier Sciences, The University of Tokyo, Kashiwa, Chiba 277-8563, Japan

coating with polymers that have high electrical polarity (Abate et al. 2010) and plasma oxidation (Kim et al. 2015), have all been used. However, these approaches have technical shortcomings, including limitation of adaptive geometry, or short lifetime and unstable wettability. In addition, control of wettability by the chemical and physical modification of the PDMS microchannel surfaces is problematic, due to the intrinsic inertness of PDMS. In contrast, glass possesses hydroxyl groups (OH), which make it suitable for surface treatment to control wettability, allowing its modification with chemicals such as silane. By using silanization (hydrophobization), Okushima fabricated a glass microchannel with local wettability control (Nisisako et al. 2005). This prepared glass microchannel enabled the formation of various droplets and particles, because of its swelling resistance (a property not exhibited by PDMS), which is an additional advantage of glass microchannels.

Octadecyltrichlorosilane (OTS) has been widely used in the hydrophobic treatment of oxide surfaces such as glass (Allara et al. 1995; Herzer et al. 2010; Manifar et al. 2008; McGovern et al. 1994; Rozlosnik et al. 2003; Sagiv 1980; Wasserman et al. 1989; Zhao et al. 2001), which can be easily hydrophobized by contact with an OTS solution or its vapor phase. Oxide surface hydrophobization using OTS results in the formation of a self-assembled monolayer (SAM) and its covalent attachment onto the surface (Sagiv 1980). According to a previous report (Pujari et al. 2014), the formation of a SAM on an oxide surface can be accomplished as follows. The glass substrate is dipped into an OTS solution that results in the hydrolysis of the OTS and replacement of the chloride atoms with hydroxyl groups to form silanol groups (Si–OH), which are hydrogen bonded to the glass substrate. Condensation then occurs between the silanol groups, resulting in the formation of siloxane bonds (Si–O–Si). The subsequent condensation between adjacent OTS silanol groups forms an OTS-SAM on the glass substrate, which contains a hydrophobic surface with long alkyl (octadecyl) groups, (Allara et al. 1995) and a hydrophilic surface bearing silanol groups. In addition, these octadecyl groups can be denatured by exposure to ultraviolet (UV) light (Masuda et al. 2003; Zhao et al. 2001). Localized UV irradiation through a photomask allows the substrate to form locally patterned hydrophobic and hydrophilic surface. Surfaces with controlled wettability have been used for applications such as the patterning of self-assembled particles on a substrate (Masuda et al. 2003) and the confinement of a liquid flow in a glass microchannel (Zhao et al. 2001). This wettability control can be used to modify a microchannel for the formation of multiple emulsion droplets, a process that requires localized wettability control. However, to date, conditions for the preparation of OTS-SAMs for controlling microchannel wettability and subsequent multiple emulsion droplet formation have not been reported.

We herein describe a method for the localized wettability control of a glass microchannel for forming multiple emulsion droplets (i.e., W/O/W and O/W/O emulsion droplets). To prepare the glass microchannel with locally controlled wettability, OTS was coated on a whole glass microchannel to promote hydrophobization, followed by local UV irradiation on the OTS-coated glass microchannel for hydrophilization. Therefore, to describe the conditions needed for the hydrophobization and hydrophilization of a glass microchannel for multiple emulsion droplet formation, we presented a model system using a glass plate and the subsequent formation of W/O/W and O/W/O emulsion droplets using a glass microchannel. In addition, the parallelized spatial wettability control of the glass microchannels was demonstrated, which enabled the generation of multiple emulsion droplets.

2 Experimental

2.1 Model system using a glass plate

Hydrophobization of a glass plate by soaking in OTS solution was conducted based on a previously reported method (McGovern et al. 1994). Prior to soaking the glass plate (glass cover, 18 mm × 18 mm, Matsunami Glass Ind., Ltd., Japan) in OTS solution, it was cleaned with an inorganic alkaline detergent (5 vol% L.G.L$_{aq}$., Yokohama Oils and Fats Industry Co. Ltd., Japan) in an ultrasonic cleaner for 5 min and then rinsed with pure water and ethanol (Wako Pure Chemical Industries, Ltd., Japan). After drying the glass plate, it was soaked in OTS solution [1 vol% OTS (Tokyo Chemical Industry Co., Ltd., Japan) in toluene (anhydrous 99.8%, Sigma-Aldrich Co. LLC., USA)] for 5 min and then rinsed with ethanol and pure water to form the hydrophobized glass plate. To evaluate the wettability of the OTS-treated glass plate surface, the contact angle of a water droplet (50 μL) on the surface was measured in air using images captured with a digital microscope (VB-6010, Keyence Co., Japan).

As previously reported, OTS-treated glass plates can be hydrophilized by exposure to UV light (Masuda et al. 2003). Thus, as described above, a glass plate was cleaned and hydrophobized with OTS. The OTS-treated glass plate was then treated with UV irradiation (specified average UV irradiation intensity of 3500 mW cm^{-2} at 365 nm, UV Spot Lightsource LC5 Lightning cure L8222-02, Hamamatsu Photonics K.K., Japan) to obtain the hydrophilized plate. The distance from the UV light source to the glass plate was ca. 1 cm. To evaluate the wettability of the

exposed OTS-treated glass surface, the contact angle of a water droplet (50 μL) on the surface was measured in air. A strong UV light source (wave length: 172 nm, intensity: ≧10 mW cm^{-2}, Min-Excimer, USHIO INC., Japan) was used for process time reduction.

2.2 W/O/W and O/W/O emulsion droplet formation using a glass microchannel

The formation of multiple emulsion droplets using a glass microchannel with locally controlled wettability was attempted. As with the glass plate, prior to hydrophobization of the fused silica glass microchannel (Figure S1), the microchannel was cleaned using an inorganic alkaline detergent in an ultrasonic cleaner for 5 min and then rinsed with pure water and ethanol. The solvents were introduced into a microchannel via polytetrafluoroethylene (PTFE) tubing (1.59 mm/0.5 mm outer/inner diameter, Flon Industry, Japan) connected to a syringe. To form the hydrophobized microchannel, the microchannel was dry-filled with OTS solution (1 vol% OTS in toluene) and then rinsed with ethanol and pure water, as above. To be consistent with the glass plate experiment, the OTS treatment time of the glass microchannel was maintained at 5 min. Since residual water in the microchannel may diminish the effectiveness of the UV treatment process, the microchannel was dried before UV exposure, blowing off any remaining water with compressed air. As previously described, the UV treatment hydrophilizes only the exposed region of the OTS-treated glass surface. Thus, to irradiate only the section of the glass microchannel requiring hydrophilization, an aluminum tape (Gun Gum Aluminum Tape, MH704, Musashi Holt Co., Ltd., Japan) was placed on the microchannel as a photomask (Fig. 1a-1, b-1). The tape position was adjusted by hand with the assistance of a microscope (IX71, Olympus Co., Japan). The OTS-treated glass microchannel was then irradiated from above (~1 cm distance) using the previously

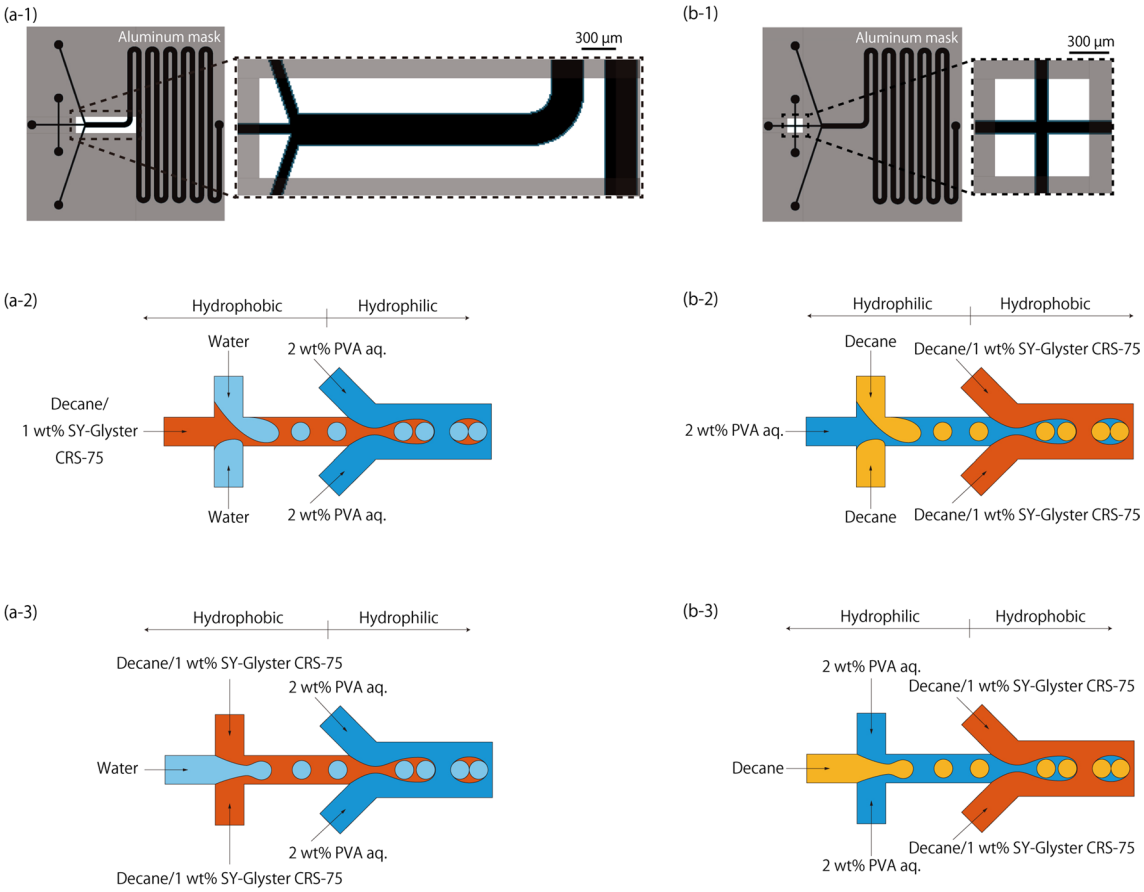

Fig. 1 Schematic of the mask position for UV irradiation of the glass microchannel, and the formation of multiple emulsion droplets using a UV-exposed glass microchannel; **a-1** mask position for W/O/W emulsion droplet formation, **a-2** alternating W/O/W emulsion droplet formation, **a-3** flow-focusing W/O/W emulsion droplet formation, **b-1** mask position for O/W/O emulsion droplet formation, **b-2** alternating O/W/O emulsion droplet formation, **b-3** flow-focusing O/W/O emulsion droplet formation

described UV source. This wettability treatment was performed before each experiment. To form the droplets, fluids were injected into the glass microchannel via both the inlet and outlet using PTFE tubing. As aqueous phases, water and an aqueous 2% polyvinyl alcohol (PVA, surfactant, hydrophile–lipophile balance (HLB) value: 18, The Nippon Synthetic Chemical Industry Co., Ltd., Japan) solution were used. As organic phases, decane and 1 wt% SY-Glyster CRS-75 (polyglycerol esters of fatty acids, surfactant, HLB value: 3, Sakamoto Yakuhin Kogyo, Osaka, Japan) in decane were used. The flow rates were controlled using syringe pumps (KDS200, KD Scientific, USA; Fig. 1a-2, 3, b-2, 3). Droplet formation was captured using a high-speed camera (FASTCAM MAX 120K or FASTCAM Mini UX50, Photron, Ltd., Japan) mounted on a microscope (BX50, Olympus Co., Japan).

2.3 Parallelized spatial wettability control of glass microchannels for multiple emulsion droplet generation

The controlled local wettability of the multiple-junction fused silica glass microchannels using the optimum conditions for the glass microchannels with a single microchannel was demonstrated. To do this, we treated four-branched glass microchannels (as shown in Fig. 4 left) with OTS followed by irradiation with localized UV through an aluminum mask. After modification of the microchannels to form multiple emulsion droplets, water was added to the microchannels (as an inner aqueous phase), together with an aqueous 2% PVA solution (as a continuous phase), and 1 wt% SY-Glyster CRS-75 in decane (as an organic phase).

3 Results and discussion

3.1 Hydrophobic and hydrophilic treatment of the glass plate

Formation of multiple (W/O/W and O/W/O) emulsion droplets using a glass microchannel requires preparation of a microchannel that exhibits locally controlled wettability. Thus, to determine the conditions required for the preparation of a glass microchannel capable of forming multiple emulsion droplets, we conducted two primary experiments: hydrophobization of a glass plate using OTS and hydrophilization of the resulting OTS-treated glass plate by localized exposure to UV light. To determine the soaking time required for hydrophobization of the glass plate, we investigated the relationship between the soaking time and wettability of the glass plate. Contact angles measured after soaking the glass plates in OTS for 2, 4, 6, 8, and 10 min were similar (Fig. 2a). Therefore, the soaking time for subsequent experiments was set at 5 min. To determine the required UV exposure time for hydrophilization of the OTS-treated glass plate, we investigated the relationship between UV light exposure time and wettability of the exposed glass plate (evaluated using the contact angle of water). Shortly after UV irradiation, the surface of the UV-exposed glass plate temporarily exhibited a significant increase in hydrophilicity. However, this higher hydrophilicity was lost upon the removal of the water droplet and subsequent application of another water droplet. Therefore, to measure the real contact angle and hydrophilicity of the UV-exposed glass plate, the first water droplet was removed, a second water droplet was placed on the

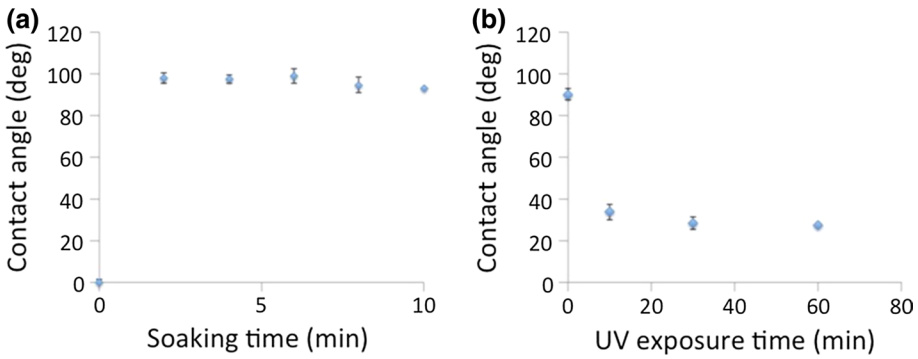

Fig. 2 Hydrophobization and hydrophilization of a glass plate; **a** relationship between soaking time and contact angle of the soaked glass plate, the contact angle at a soaking time of 0 min is the contact angle of the virgin glass plate, each point is an average of five measurements; **b** relationship between UV exposure time and contact angle of the glass plate soaked first in OTS for 5 min and then exposed to UV irradiation, contact angle with a UV exposure time of 0 min indicates the contact angle of an OTS-treated glass plate without UV exposure, each point is an average of five measurements

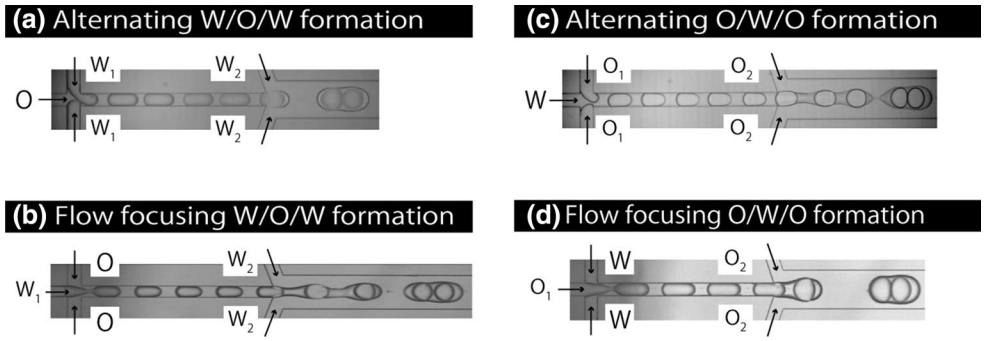

Fig. 3 Multiple emulsion droplet formation using glass microchannels treated using OTS and by UV irradiation; **a** alternating W/O/W formation (O: 1 mL h^{-1}, W_1: 1.5 mL h^{-1}, W_2: 8 mL h^{-1}), diameter of a droplet of the innermost liquid phase was 161 ± 0.8 μm [a coefficient of variation (CV): 0.5%]; **b** flow-focusing W/O/W formation (O: 2.5 mL h^{-1}, W_1: 5 mL h^{-1}, W_2: 13 mL h^{-1}), diameter of a droplet of the innermost liquid phase was 152 ± 0.8 μm (CV: 0.5%); **c** alternating O/W/O formation (W: 3 mL h^{-1}, O_1: 2 mL h^{-1}, O_2: 13 mL h^{-1}), diameter of a droplet of the innermost liquid phase was 151 ± 0.9 μm (CV: 0.6%); **d** flow-focusing O/W/O formation (W: 2 mL h^{-1}, O_1: 8 mL h^{-1}, O_2: 8 mL h^{-1}), diameter of a droplet of the innermost liquid phase was 175 ± 0.9 μm (CV: 0.5%), each solution introduced into the microchannel corresponds to those shown in Fig. 1

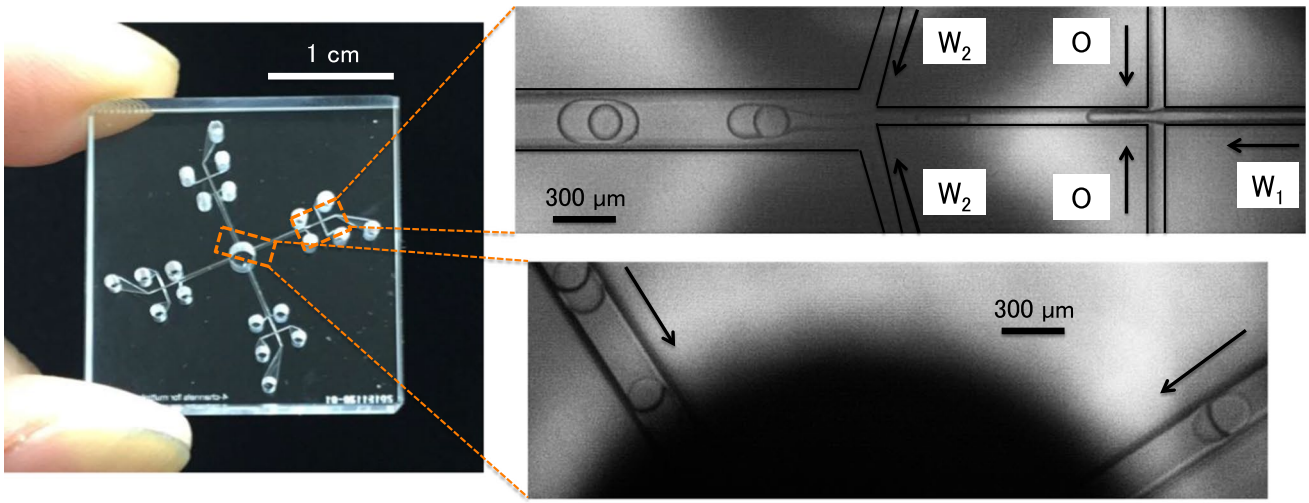

Fig. 4 Multiple emulsion droplet generation in glass microchannels with multiple junctions, four-branched glass microchannels (*left*), and multiple emulsion droplet generation on the treated microchannels (W_1: 3 mL h^{-1}, W_2: 20 mL h^{-1}, O: 4 mL h^{-1}; *right*), each solution (W_1, W_2, and O) introduced into the microchannel corresponds to those shown in Fig. 1a-3

surface, and the contact angle was measured. With a UV exposure time of 10–60 min, the wettability stabilized (contact angle: 27 ± 2.9; Fig. 2b). This demonstrated that continuous exposure of an OTS-hydrophobized glass surface to UV irradiation yields stable hydrophilicity and wettability. The surface could be reused after one application, because the surface exposed to water was sufficiently hydrophilic to produce a droplet and the contact angles obtained by repeat measurements were relatively constant. The surface of the glass plate after OTS/UV treatment was as smooth as that of the non-treated glass plate (Figure S2).

3.2 Hydrophobic and hydrophilic treatment of a glass microchannel and multiple emulsion droplet formation

The formation of multiple emulsion droplets using a glass microchannel requires a microchannel with locally controlled wettability. The preparation of such a

wettability-controlled glass microchannel was obtained by the hydrophobization of a glass microchannel using OTS, followed by local hydrophilization of the OTS-treated glass microchannel by UV irradiation. Conditions optimized using the glass plate (see above) were applied in this experiment. We investigated the possibility of the formation of multiple (W/O/W and O/W/O) emulsion droplets with respect to UV exposure time. With a UV exposure time of 6 h, the dispersed phase wetted the microchannel surface (Figure S3) due to insufficient treatment time. Therefore, attempts were made to improve the conditions with a longer exposure time of 12 h. The in-channel contact angle measurement, obtained using a method reported by Tan et al. (2010), was 22° ± 3.3° (Figure S4). The resulting measurements were suitable for the production of multiple emulsion droplets, and this result agreed with the reported results. In other words, multiple emulsion droplets could be formed by PDMS microchannels with 180 s of plasma treatment (Kim et al. 2015) and PDMS microchannels with the 200 s plasma treatment had in-channel contact angles of approximately 20° (Tan et al. 2010). This glass microchannel allowed the generation of alternating and flow-focusing W/O/W and O/W/O emulsion droplets (Fig. 3). The W/O/W emulsion droplet was stable in both hydrophobic and hydrophilic areas of the microchannel, and the device could be used to produce multiple emulsion droplets for at least 12 h.

To obtain sufficient wettability of the glass microchannel to generate multiple emulsion droplets, a longer UV irradiation time was required than that used for the glass plate. This was due to the transmission of the UV irradiation through the glass (thickness: ca. 1.5 mm) rather than directly onto the glass, resulting in the exposure of the channel walls. In addition, the glass microchannel treated using this method could be used to generate W/O/W and O/W/O emulsion droplets one week after UV irradiation when it was wrapped in an aluminum foil and stored at room temperature. According to a published report (Tan et al. 2010), the hydrophilicity of a device stored in water can be maintained for weeks or more. To confirm if this was the case with the device treated using our method, the maximum time that a device stored in water (as well as in air) can remain usable for the production of a droplet will be investigated in a future work.

We confirmed the long-term storage stability of the W/O/W and O/W/O emulsion droplets. In this case, in a commonly used procedure, a surfactant with a low HLB was added to the oil phase, and a surfactant with a high HLB was added to the aqueous phase (as described in the Experimental section). Stored droplets retained the form of W/O/W and O/W/O emulsion droplets for several days (Figure S5). In addition to this result, the generation of multiple emulsions was dominated and controlled by a number of parameters, including the flow rates of the dispersed and continuous phases, viscosity, and interfacial tension of fluids introduced to the microchannel and channel geometry. Therefore, a comprehensive investigation into the different experimental conditions will be performed in the near future.

3.3 Parallelized spatial wettability control of glass microchannels for multiple emulsion droplet generation

We also demonstrated the formation of multiple emulsion droplets using glass microchannels with multiple junctions, whose wettability was locally controlled. By introducing each solution into the microchannels at constant flow rates, we successfully generated multiple emulsion droplets on the treated microchannels with multiple junctions (Fig. 4, right). In a previous study, glass microchannels with multiple junctions have been developed for producing organic multiple emulsion droplets, such as oil-in-oil-in-oil (O/O/O) emulsion droplets (Nisisako et al. 2012). However, the formation of aqueous-phase-containing double emulsion droplets, such as W/O/W emulsion droplets, in glass microchannels with multiple junctions has not been established. In contrast, our technique enabled the formation of these droplets.

3.4 Processing time reduction using a strong UV light source

To reduce the processing time, we used a strong UV light source and confirmed that the microchannel treated with this source could be used for droplet formation using an experimental procedure similar to Figure S3. A microchannel irradiated by a strong UV light source (which was set at ~1 cm above the microchannel) for 10 min could stably form a droplet, while wetting was observed in a microchannel that had been irradiated for 5 min (as is the case with Figure S3). This showed that irradiating with a 172 nm UV light for 10 min was beneficial for rapid hydrophilization of a fused silica glass microchannel treated with OTS.

4 Conclusion

We herein described a method for the preparation of a glass microchannel capable of forming multiple emulsion droplets through local control of the wettability of the glass microchannel. This method for wettability control is simple and consists of two main steps: (1) hydrophobization of a glass microchannel by filling it with an OTS solution for 5 min and (2) local hydrophilization of the OTS-treated

glass microchannel by UV irradiating through a mask for 12 h (UV light source ~1 cm above the microchannel). When a strong UV light source was used, the UV exposure time could be reduced to 10 min. In addition, use of glass microchannels with multiple junctions treated by this method allowed the formation of multiple emulsion droplets in each multiple junction. The glass microchannel prepared according to this method enabled the generation of various aqueous and organic droplets due to its resistance to swelling.

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