Master's Thesis
석사 학위논문

A Poly(dimethylsiloxane) Microfluidic Channel Coated with Poly-p-xylylene for Nanocrystal Growth Applications

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Co-advisor : Professor Taejoon Park

by

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A thesis submitted to the faculty of DGIST in partial fulfillment of the requirements for the degree of Master of Science in the Department of Robotics Engineering. The study was conducted in accordance with Code of Research Ethics[1)].

01. 10. 2014

Approved by

Professor SangJun Moon (Signature)
(Advisor)

Professor Taejoon Park (Signature)
(Co-Advisor)

[1)] Declaration of Ethical Conduct in Research**:** I, as a graduate student of DGIST, hereby declare that I have not committed any acts that may damage the credibility of my research. These include, but are not limited to: falsification, thesis written by someone else, distortion of research findings or plagiarism. I affirm that my thesis contains honest conclusions based on my own careful research under the guidance of my thesis advisor.

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Heejin Lim

Accepted in partial fulfillment of the requirements for the degree of Master of Science.

12. 03. 2013

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ABSTRACT

Applications of microfluidic device fabricated in poly(dimethylsiloxane) (PDMS) have been limited to water-based analysis rather than nonpolar solvent based chemistry due to PDMS swelling problem occurring by absorption of the solvents. The absorption and swelling causes PDMS channel deformation in shape and changes the cross sectional area, making it difficult to control the flow rate and concentrations of solution in PDMS microfluidic channels. We propose that poly-p-xylylene polymers (parylenes) were chemical vapor deposited on the surfaces of PDMS channels to alleviate the effect of solvents on the absorption and swelling. The parylene coated surface sustains 3hours with a small volumetric change (less than 22% of PDMS swelling ratio). By generating an air-nonpolar solvent interface based on droplets in PDMS channel, we confirmed poly-p-xylylene coated PDMS microfluidic channels have the potential to be applicable to nanocrystal growth using nonpolar solvents.

Keywords: Poly(dimethylsiloxane), PDMS, Microfluidic channel, Poly-p-xylylene, Parylene, Nanocrystal growth

Contents

List of Figures

1. INTRODUCTION

1.1 Motivations

Advances in medical technology have contributed to an aging society, prompting needs of health care and welfare of the aged. At the same time, the remarkable increase in an aged population suffering from neurodegenerative disease has been a worldwide issue; Alzheimer's disease (AD) as a neurodegenerative disease causes dementia and pains over 35.6 million people throughout the world, which generates economical costs, more than US $604 billion in 2010 [1, 2].

It has been reported that neurodegenerative disease is mainly attributed to damage to neuronal networks [3, 4] or synaptic dysfunction [5-7]. To identify the damage, it needs to research from single neuronal synapse to complex neuronal network. Neuronal networks and connectivity in the human brain are extraordinarily complex and far-reaching. In addition, the complex neuronal cytoarchitecture incorporates large numbers of neurons which are extended and highly branched, provoking innumerable synaptic formations to connect with other neurons extensively and packing all the space available in the brain [8, 9]. Consequently, research into neuronal networks *in vivo* has encountered obstacles by such a complex microenvironment. To simplify the networks, first petri dish based method has been suggested and used for simple research tool. Conventional *in vitro* method of culturing neurons on a planar plastic dish has prevailed among scientists to study neuronal dynamics, contributing to excellent understanding of the neuronal and synaptic biology [10, 11]. Nonetheless, the petri dish based neuronal culture that merely provides homogeneous environments is not an appropriate model for subcellular analysis of individual neurons residing in varying extracellular microenvironments; therefore, novel technologies have been emerging to

overcome the aforementioned limitation by manipulating neuronal microenvironments and localizing interactions of individual neurons [1, 12, 13].

Over the past few years, microfluidic based technologies have stimulated several attempts to culture neurons in microfluidic devices and control microenvironment in a spatiotemporal method. Since the development of a microfluidic multi-compartmentalized device incorporating two fluidically isolated compartments which are connected each other with microgrooves, its modified designs have been widely applied to various neuronal research [14-16]. These devices have been successfully used to long term culture neurons and direct axons to an independent place isolated from soma, thereby facilitating local subcellular analysis. Moreover, not only axon guidance was controlled, but dendrites were directed to extend into microgrooves and connected to axons grown from the opposite side; synapses were formed in the local perfusion channel intersecting microgrooves [17].

1.2 Objectives and Problem

Poly(dimethylsiloxane) (PDMS) has been of interest to many researchers in the field of microfluidics because it has several advantageous characteristics. For instance, it is easy to fabricate, optically transparent, biocompatible, and inexpensive [18-20]. Despite these advantages, applications of microfluidic devices fabricated in PDMS have not been applicable to bioanalysis using small molecules which are absorbed and dispersed into PDMS due to its porous property [21, 22]. The absorption property of PDMS makes it difficult to conduct intensity-based bioanalysis using hydrophobic fluorescent dyes ranging from Nile red [22] to Rhodamine B (RhB) [23] due to the increased background noise signals of the targeted molecules [22]. In an effort to overcome the PDMS absorption problem, the surfaces of the PDMS should be provided with a thin protective layer, which can preclude PDMS from sucking up small molecules. Over the past few years, poly-p-xylylene polymers (parylene) have been recognized as a potential thin film that can be uniformly coated onto PDMS surfaces due to its non-porous and transparent characteristics [24-26]. It has been reported that parylene can be used to enhance the surface properties of PDMS microfluidic devices to block the absorption of fluorescent dyes [27], proteins and DNA [28].

Regarding the application of PDMS microfluidic devices to areas of nonpolar solvent-based chemistry such as nanoparticle synthesis [29-32], the shortcomings of PDMS are more likely to stand out because PDMS given its porous nature not only absorbs nonpolar solvents but even swells in volume [21, 33]. The natural surface of PDMS microfluidic devices does not provide an environment for nanoparticle synthesis in which tiny amounts of liquids and concentrations should be precisely controlled. As an organic solvent absorbed into the PDMS wall induces swelling in the PDMS, it leads to a concentration change between the nanoparticles dispersed in the solvents and the precipitant. In addition, the deformation of the

channel by swelling affects the flow rate because it changes the cross-sectional area. Numerous attempts have been made to solve the PDMS swelling problem with chemically resistant materials such as Viton, CYTOP, Chemraz [34] and Teflon [35] used as coatings. Although these approaches have improved the PDMS surface properties to some extent, they have not solved the PDMS swelling problem completely [21, 34]. Moreover, these materials could not conformally coat the 3D surface of the microfluidic channel. On the other hand, a polytetrafluoroethylene (PTFE, called DuPontTM Teflon®) capillary tube is inserted and assembled with a chip to prevent the concentration changes and unstable flow rates, as Teflon® has strong chemical resistance to nonpolar solvents, as shown in Figure 1-1a. The fabrication method implies that a PDMS microfluidic device can be applied for the growth of nanocrystals localized in nanoliter droplets [30]. However, the tubing process is burdensome and time-consuming due to the additional alignment necessary for the microscopic assembly between the channel and the Teflon capillary tube.

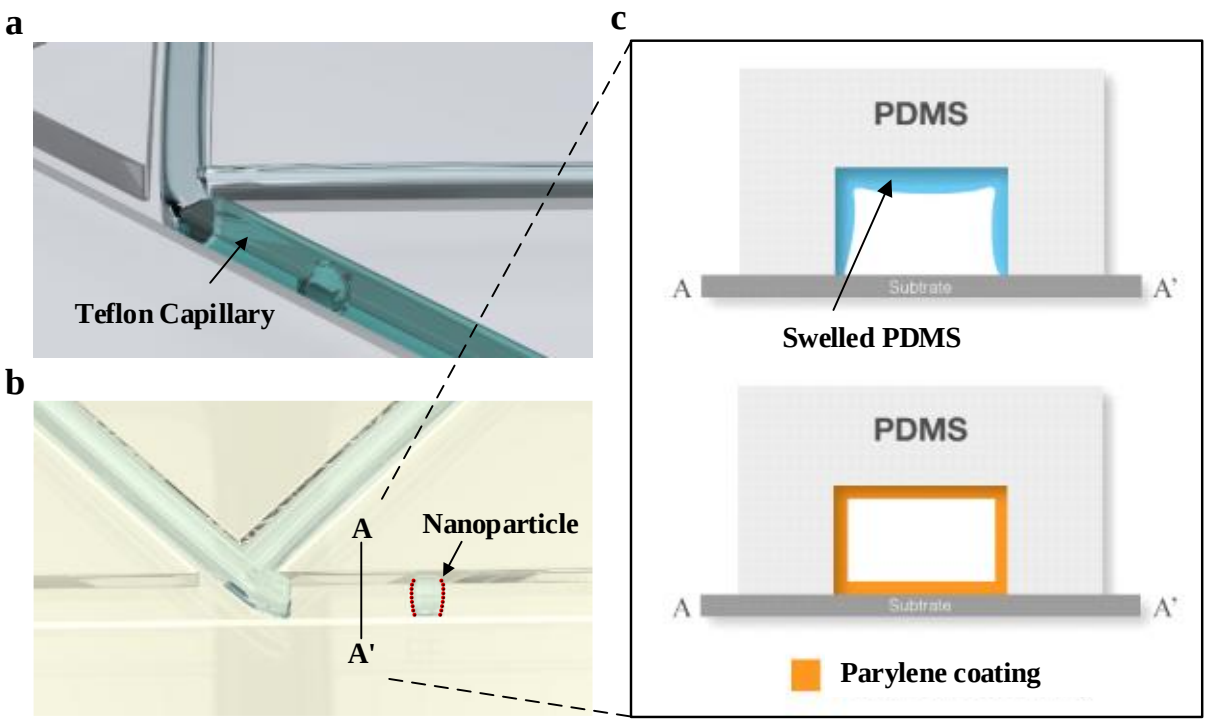

Figure 1-1. Parylene coated PDMS microfluidic channel overview

A parylene coated PDMS microfluidic device can be applied for the synthesis of nanocrystals which is conducted at non-polar solvent environment in nanoliter droplet without swelling of a microfluidic channel surface. (a) Assembly of a chemically resistant capillary (e.g., Teflon®) with a PDMS channel is necessary for nonpolar-solvent-based nanocrystal growth. (b) A chemically resistant material such as parylene should be coated onto the surfaces of PDMS without a Teflon capillary. (c) Schematic cross-sectional illustrations of the nonpolar solvent effect in the PDMS channel and in parylene-coated PDMS. Chemical reactions of a nonpolar solvent with polymerized PDMS lead to PDMS swelling. The channel deformed by swelling in the solvents has an effect on the flow rate as it changes the cross-sectional area, but a thin parylene film deposited onto the PDMS surfaces prevents the swelling and makes it possible to maintain a flow rate constant.

1.3 Hypothesis

To overcome the problems of PDMS swelling and the requirement of an additional assembly process, we applied a non-porous and transparent polymer film, parylene, which has high chemical resistance and which can be coated by chemical vapor deposition (CVD) onto surfaces with relatively complex geometries. In addition, a parylene film can cover even an inside PDMS microchannel by means of a gaseous deposition process. Parylene coating inside a PDMS microfluidic channel has been well characterized in studies of the quality of coated parylene films thickness on inner PDMS walls in the literature [36]. The non-porous parylene film serves as a chemically resistant barrier to prevent the PDMS from deformation when it comes in contact with solvents, as shown in Figure 1-1b-c. Although parylene does not permanently cover the PDMS surface to block the swelling, the duration of its resistance to a nonpolar solvent appears to be feasible for a nanocrystal synthesis process which requires less than one hour [29, 31, 32]. To verify the chemically resistant characteristics of a parylene-coated microfluidic channel, we carried out a swelling test of parylene-coated PDMS in contact with a nonpolar solvent which is used for nanocrystal growth (e.g. toluene). To apply our device in further fields using nonpolar solvents at the toluene-air interface such as a monolayer of charged gold nanoparticles self-assembly, we fabricated a simply designed PDMS microfluidic channel to generate a droplet-based air-toluene interface [29, 31, 32]. Consequently, we determined the potential of a parylene-coated monolithic PDMS microfluidic device to be robust against a nonpolar solvent while also being easy to fabricate and simple to process for nanocrystal growth applications.

1.4 Background Information

1.4.1 Microfluidic platforms

In the microfluidic field, researcher have tried to fabricate devices with micro scale channels capable of manipulating a small volume of fluids [37, 38]. Microfluidic chips facilitate the building of desired microenvironments for culturing cells [39] and growing nanocrystal superlattices [30] as well. The fabrication of microfluidic platforms mainly takes advantage of photolithography by which SU-8 negative photoresist is exposed by ultraviolet (UV) beam passing through a patterned mask and polymerizes to form a hard master. In addition, soft lithography uses the fabricated master as a replica mold into which elastomeric polymer poly(dimethylsiloxane) (PDMS) is poured, creating microfluidic devices in a reproducible way. In general, PDMS is the most fundamental material due to its outstanding characteristics: biocompatibility, gas permeability, optical transparency, easy of fabrication, and low cost [40, 41].

2. MATERIALS AND METHODS

2.1 Microfluidic Devices

2.1.1 PDMS microfluidic chip fabrication (Paper based master)

We designed a PDMS straight channel with two reservoirs and a PDMS microfluidic based droplet generator which were fabricated rapidly using a sheet based master and soft lithography. First, a silicon wafer is placed in a glass dish, and then the channel-patterned adhesive sheets that are cut with a cutting plotter (CE5000-40, Graphtec, Japan) are attached to imprint the pattern onto the silicon wafer surface. After mixing the PDMS base solution and the curing agent (Sylgard® 184, Dow Corning, Korea) together in the ratio of ten to one, the mixed PDMS solution is the poured into a glass dish. A desiccator (AS.1-068-01, As One, Japan) is used to remove the dissolved gas from the mixed PDMS solution and curing the mixed PDMS solution is achieved by heating the solution in the oven in 70℃ for 2 hours (JSOF-150, JSR, Korea). When the PDMS solution is solidified, the desired part of the cured PDMS is cut out using a surgical knife (Handle: HA.HSB805.03, Blade: HA.HSB705.11, Karl Hammacher GmbH, Germany). An inlet for inflow of the fluid and an outlet for outflow of the fluid are punched in the PDMS channel with a micro-punch (ID: 0.75mm, OD: 1.07mm, Prod No. 15072, Harris Uni-CoreTM, USA). Then the PDMS channel is placed on a slide glass, and they bond together by a plasma system (CUTE-B, FemtoScience, Korea) that generates oxygen plasma (20s, 40W). Lastly, microbore tubes (ID: 0.254mm, OD: 0.762mm, T23-140-700/AAQ040109, TygonTM, USA) are connected into the inlet/outlet of the PDMS channel and syringe pump equipped with syringes (30Gauge, ID: 0.140mm, OD: 0.305mm)

2.1.2 PDMS microfluidic chip fabrication (Photolithography)

A PDMS microfluidic chip was fabricated using soft-lithography. HMDS (HexaMethylDiSilazane), a pre-treatment of the silicon wafer for obtain maximum process reliability, was done first. SU-8 2050 (MicroChem) was spin-coated on a 4-inch silicon wafer at 500 rpm for 5sec and 3000 rpm for 60 sec to obtain 50μm thickness. And then PR spin-coated wafer was baked at 60℃ for 3 min and 95℃ for 7 min in a convention oven. The soft-baked wafer was exposed to UV light for 12 sec at 310 mJ/cm2 under the photofilm mask and basked at 65℃ for 1 min and 95℃ for 8 min in a convention oven. The hard baked SU-8 2050 was developed in SU-8 developer for 6 min, rinsed with de-ionized (DI) water and blow-dried with nitrogen gas finally. First PDMS mold in a glass dish and a few drop of silanizing reagent, Trimethoxy (3, 3, 3-trifluoropropyl) silane (Cat. 9187, Sigma) in a glass bottle were placed in vacuum desiccator with for 2 hour for silanization of the surface of the mold. The PDMS pre-polymer based solution and curing agent (Sylgard-184, Dow Corning, Korea) are mixed at a 10:1 weight ratio and poured over the silanized PDMS master with 5 mm thickness. The degassing process in vacuum chamber for an hour was removing dissolved gas from the mixed PDMS solution and curing the mixed PDMS solution is achieved by an oven (70℃ for 2 hours, JSOF-150, JSR, Korea). When the PDMS solution is solidified, desired part of the cured PDMS that is defined as the PDMS channel was cut out using a surgical knife. Then the PDMS channel and slide glass bonded together by a plasma system (CUTE-B, FemtoScience, Korea) that generates oxygen plasma (generating time: 20s, generator power: 40W).

2.2 Parylene-C film on PDMS Surfaces

2.2.1 Parylene-C coating

A parylene film coater (LAVIDA-220, FemtoScience, Korea) was used to coat parylene-C film onto the inside of the PDMS microfluidic channel. Parylene-C dimer (Nuri-Tech, Korea) is vaporized by sublimation in a vacuum pressure (~ 133Pa) set to 150℃, becoming a gaseous precursor for the parylene-C film. The dimer in the gas phase is cleaved into two monomers at a temperature exceeding 680℃ in a pyrolysis furnace. Gaseous monomers diffuse into the deposition chamber and flow deep inside the microfluidic channel through the inlet and outlet so that all the surfaces of the chip are exposed to gaseous monomers and coated with non-porous parylene-C film by polymerization at room temperature below a pressure of 13.3Pa, as shown in Figure 2-1. The process performed at room temperature for parylene polymerization is an attractive characteristic because a parylene film can be coated even onto thermally sensitive materials.

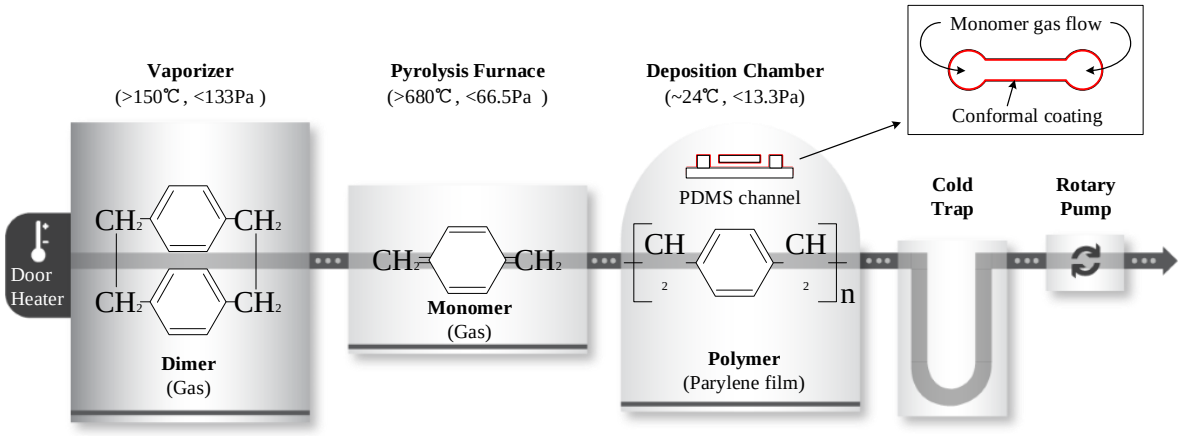

Figure 2-1. Parylene-C coating using chemical vapor deposition (CVD) process

Parylene-C is deposited in manner of chemical vapor deposition (CVD) process in a vacuum environment consisting of a vaporizer, a pyrolysis component, and a deposition chamber. The dimer is vaporized through sublimation at 150℃, becoming the gaseous precursors of the parylene-C film. The vaporized dimer is broken into two monomers by pyrolysis at 680℃ in the pyrolysis chamber. The monomer gas diffuse into the deposition chamber and can pass through the microfluidic channel in vacuum environment which gives a conformal coating of a complex 3D microfluidic surface. On the surface of the substrate at room temperature and below a pressure of 13.3Pa, the polymerization of the monomers leads to a thin and non-porous parylene film.

2.2.2 Thickness and porosity measurements

The thickness of polymerized parylene-C is linearly related to amount of solid dimer put into the vaporization chamber. We used four different amounts of dimer (10, 20, 30 and 40g) for the thickness measurement. Adhesive tape is attached on a part of slide glass used as a substrate before the parylene coating. The substrate was coated with parylene-C then, the previously attached tape was peeled off together with coated parylene film on the tape. The thickness of the parylene film on the substrate was measured using a surface profiler. On the other hand, we used a few different deposition rates for the porosity measurements. The porosity was measured using a scanning electron microscope and an atomic force microscope.

2.2.3 Swelling measurements

Samples for the swelling test were prepared after parylene-C was coated onto hexagonally shaped PDMS pieces to measure the ability of the parylene-C film to block the PDMS swelling in nonpolar solvents such as toluene (244511, SIGMA, Korea). The swelling measurements of both the non-coated PDMS and the parylene-coated PDMS were carried out using a previously reported method [33]. Briefly, hexagonally shaped pieces in PDMS were cast from a mold fabricated by a rapid prototyping (RP) process using the 3D printer (uPrint SE, Stratasys, USA). The PDMS hexagon pieces with or without the parylene film coating were immersed in toluene for 10hours at room temperature. Images of the PDMS were captured with a digital single-lens reflex camera (DSLR7000, Nikon, Japan) every hour and the dimensional lengths changed by swelling were measured by an image-processing method which can depict the outline of the hexagonal shape determined by a threshold value of the image intensity. To normalize the swelled extent of PDMS, we used a swelling ratio defined in the literature [33], which is a ratio of the length between the opposite edges of a PDMS hexagon after it is immersed in toluene to its original length before immersion as shown in Figure 3a.

A PDMS straight channel with a width of 250μm was fabricated to study the effect of a nonpolar solvent on the inner wall of the PDMS channel. Two reservoirs were punched at either end of the channel with a micro-punch so that the straight channel would act as a bridge which connects the reservoirs, which were then filled with solvents. The solvents in the reservoirs spontaneously flow into the channel by capillary action. The solvent should be consistently provided by dropping it onto the two reservoirs at a low flow rate because the solvent tends to dry and absorb into the PDMS surface over time. The straight PDMS channel was observed under an inverted microscope (IX71, Olympus, Japan) and images of the PDMS channel deformed by solvents were captured using a still camera (E-PL3, Olympus, Japan).

2.2.4 Air-nonpolar solvent interface formation

Using the T-shaped and coated with parylene-C microfluidic device, an air-nonpolar solvent interface was formed in the channel. The T-shaped channel consists of a carrier channel with a width of 500μm and an injection channel with a width of 250μm as shown in Figure 3-5. These channels were connected perpendicularly to form a micro bubble. Toluene as a nonpolar solvent is flowed into the carrier channel at a flow rate of 500μl/h and air is pumped into the injection channel at 250μl/h. Both flow rates were controlled by one syringe pump each (Fusion 100 Touch, Revodix, Korea). As air flow enters the carrier channel and meets nonpolar solvent flow, the air flow is deformed in the direction of the solvent flow and finally separated into air droplets. By constantly generating arrays of air droplets along the carrier channel, the nonpolar solvent is also separated between two successive air droplets, forming air-nonpolar solvent interfaces in the channel.

2.3 Gold Nanoparticle Synthesis

2.3.1 Materials

The following chemicals were used as obtained: $HAuCl_4 \cdot 3H_2O$ (520918), toluene and hexane from Sigma-Aldrich; Sodiium borohydride granules 98% ($NaBH_4$, 7537-1425), 1N-Hydrochloric acid standard solution (HCl, 4095-3700), 1N-Sodium hydroxide standard solution (NaOH, 7576-3700), and 1-dodecanethiol 98% (3102-4400), acetone from DAEJUNG; Deionized (DI) water with a resistivity of 18.2 MΩcm was used.

The following processes was conducted as a beginning step. DI water, acetone, and hexane was stored in a 250ml beaker each for cleaning. As used for Au nanoparticle synthesis, acetone and hexane was stored in a washing bottle each as well. 1-dodecanethiol was stored in a 1ml syringe to be used during a nanoparticle process. For 20ml of 50mM HCl solution, 1ml of 1M HCl was mixed with 19ml of DI water by a vortex for 10sec. For 20ml of 50mM NaOH solution, 1m of 1M NaOH was mixed with 19ml of DI water by a vortex for 10sec. 50mM gold chloride anions ($AuCl_4^-$) and 50mM borohydride anions (BH_4^-) was prepared as shown in Figure 2-2. To be specific, 50mM gold chloride anions ($AuCl_4^-$) was obtained by adding 0.394g of $HAuCl_4 \cdot 3H_2O$ to 20ml of 50mM HCl solution and by mixing them with a vortex for 60sec. 50mM borohydride anions (BH_4^-) was obtained by adding 75.66mg of NaBH4 granules to 40ml of 50mM NaOH solution and by mixing them with a vortex for 60sec.

a

b

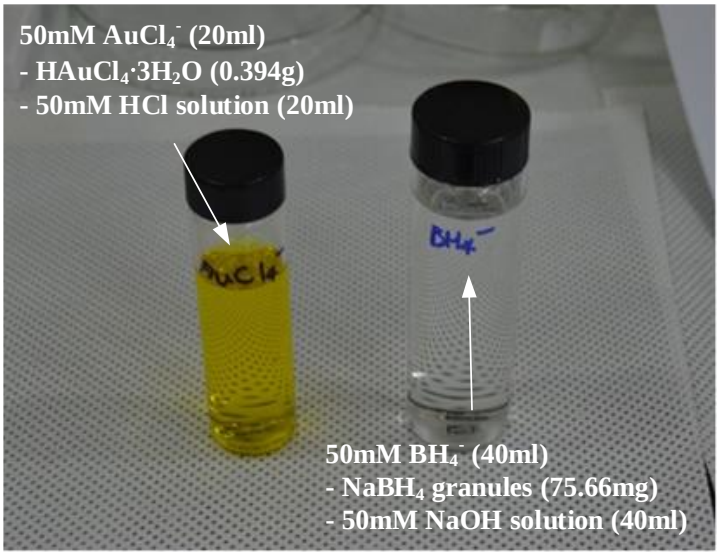

Figure 2-2. Materials and preparations for 50mM gold chloride anions ($AuCl_4^-$) and 50mM borohydride anions (BH_4^-)

Materials and processes were prepared for gold nanoparticles synthesis. (a) Materials as used for 50mM HCl solution, 50mM NaOH solution, 50mM gold chloride anions, and 50mM borohydride anions. (b) 50mM gold chloride anions ($AuCl_4^-$) was obtained by adding 0.394g of $HAuCl_4 \cdot 3H_2O$ to 20ml of 50mM HCl solution and by mixing them with a vortex for 60sec. 50mM borohydride anions (BH_4^-) was obtained by adding 75.66mg of NaBH4 granules to 40ml of 50mM NaOH solution and by mixing them with a vortex for 60sec.

2.3.2 Synthesis of nanoparticles in water

An aqueous stock solution of 50mM gold chloride anions ($AuCl_4^-$) in a glass vial was made by dissolving 0.394g of $HAuCl_4 \cdot 3H_2O$ with 20ml of 50mM HCl, ensuring stability for more than several months. An aqueous stock solution of 50 mM borohydride anions (BH_4^-) in a glass beaker was made by dissolving 75.66mg $NaBH_4$ granules with 40ml of 50mM NaOH, guaranteeing stability for several hours at room temperature. For the nanoparticles of 5.2nm in diameter, we added 100μl of the $AuCl_4^-/H^+$ solution to a glass vial with 9g of DI water and later injected 650μl of the BH_4^-/OH^- solution all at once, while stirring on a vortex for uniform mixing as shown in Figure 2-3. The total weight of the aqueous solution was controlled to be 10g so that the concentrations of gold ions is 0.50mM. The solution changed color from light yellow to orange immediately, and then to red while the vial was stirred for 1 min to release hydrogen gas molecules. After 1 min shaking, the vial was heated at 250℃ for 180s. For nanoparticles of other sizes, the amount of the BH_4^-/OH^- solution was increased from 300 to 650μl followed by heating for 2-3min at the boiling temperature of water on a hot plate. The average diameter of gold nanoparticles was precisely controlled from 3.2 to 5.2nm by changing the amount of the BH_4^-/OH^- solution 300 to 650μl as shown in Table 2-1.

2.3.3 Phase transfer of nanoparticles to hexane

Phase transfer of nanoparticles to hexane was conducted as shown in Figure 2-4. 5.0g acetone was added to the 10g aqueous solution of gold nanoparticles and mixed by hand for 1s, immediately after which 5.0g of hexane with two droplets of DDT was added, and then the vial was shaken vigorously by hand for 30s. The water-acetone phase became colorless, and the hexane phase turned dark red due to the phase-transfer of gold nanoparticles. No postsynthesis cleaning step was employed, since all reaction byproducts remain in the water-acetone phase. Gold nanoparticles in hexane are stably dispersed for longer than several months.

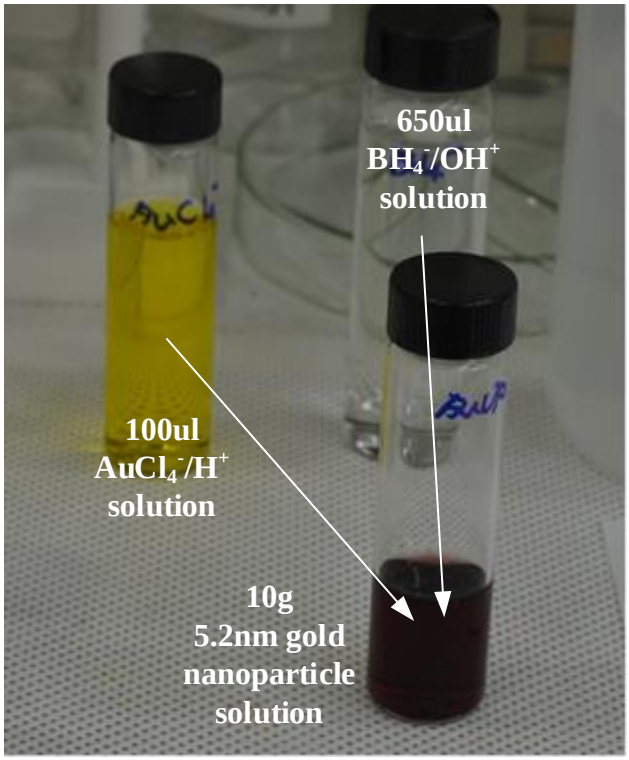

Figure 2-3. Synthesis of gold nanoparticle with 5.2nm diameter in water

For the nanoparticles of 5.2nm in diameter, 100μl of the $AuCl_4^-/H^+$ solution and 650μl of the BH_4^-/OH^- solution was added to 9g of DI water stirring on a vortex for uniform mixing. The total weight of the aqueous solution was controlled to be 10g so that the concentrations of gold ions is 0.50mM. The solution changed color from light yellow to orange immediately, and then to red while the vial was stirred for 1 min to release hydrogen gas molecules. After 1 min shaking, the vial was heated at 250℃ for 180s.

Table 2-1. Four different sizes of gold nanoparticles depending on the amount of solutions

$AuCl_4^-/H^+$	BH_4^-/OH^-	Au Nanoparticle Size
100μl	300μl	3.2nm
	425μl	4.8nm
	575μl	4.2nm
	650μl	5.2nm

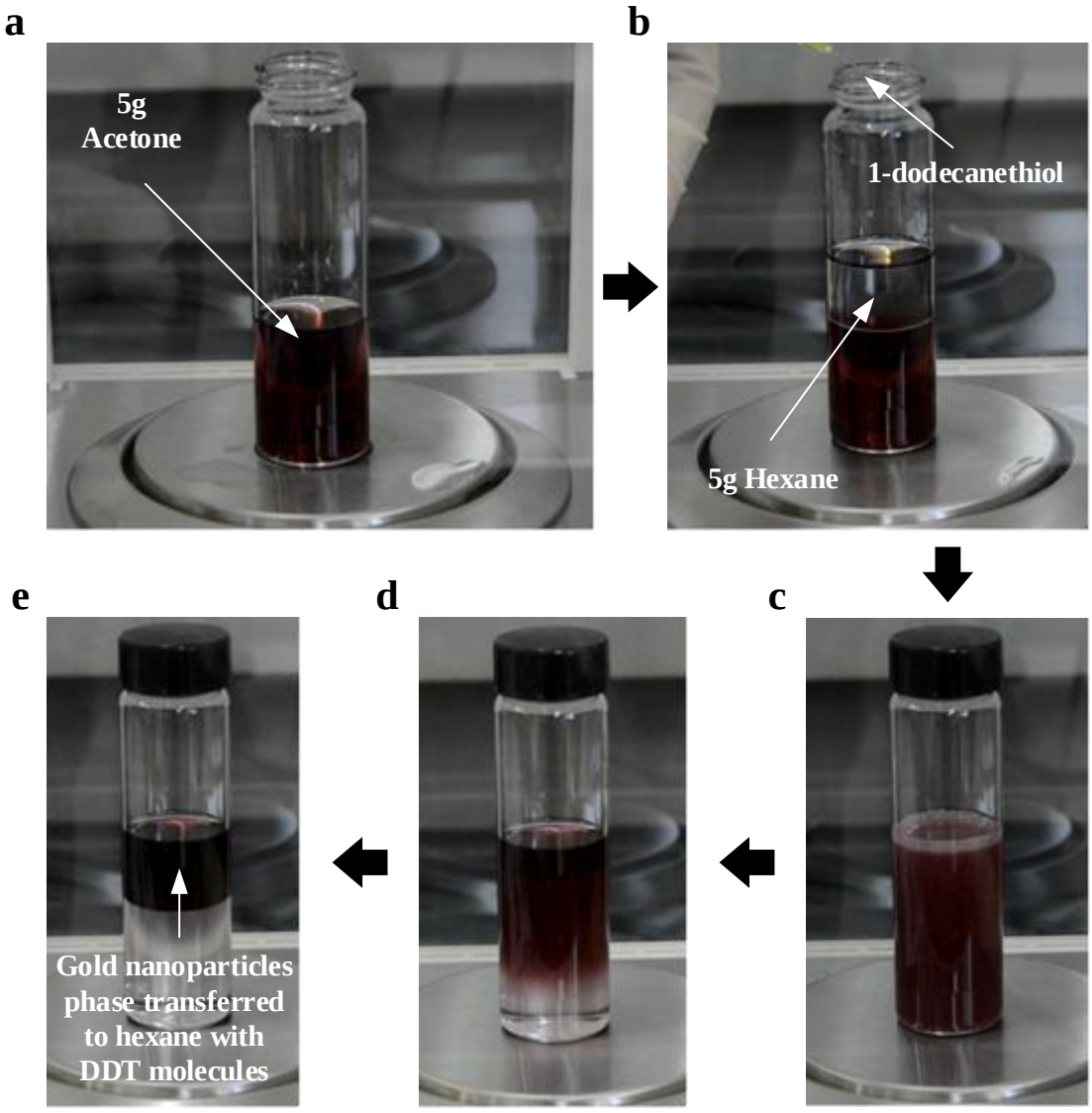

Figure 2-4. Phase transfer of gold nanoparticles with 1-dodecanethiol to hexane

(a) 5.0g acetone was added to the 10g aqueous solution of gold nanoparticles and mixed by hand for 1s. (b) 5.0g of hexane with two droplets of 1-dodecanethiol stored in a 1ml syringe was added, and then the vial was shaken vigorously by hand for 30s. (c) Gold nanoparticles were dispersed throughout the solution. (d) The water-acetone phase became colorless and gold nanoparticles coated with DDT molecules were transferred to hexane. (e) The hexane phase turned dark red due to the phase-transfer of gold nanoparticles.

2.3.4 2D self-assembly of gold nanoparticles

A hexane droplet containing gold nanoparticles was deposited to a larger toluene droplet on a piece of Teflon plate to compare a hexane droplet containing gold nanoparticles just on a Teflon plate as shown Figure 2-5. Hexane evaporates ~4 times faster than toluene. With a 10mm diameter toluene droplet, the toluene evaporation and deposition of a monolayer film of nanoparticles took ~10 min in a fume hood. The interior of the hexane-toluene droplet became colorless immediately and the surface became purple. If the volume ratio of toluene to hexane is smaller, the floating of nanoparticles to the air-liquid interface takes slightly longer. If a hexane droplet containing gold nanoparticles was directly dropped onto a piece of Teflon plate, its color remained red throughout the evaporation, implying that gold nanoparticles were kept dispersible within the shrinking hexane droplet.

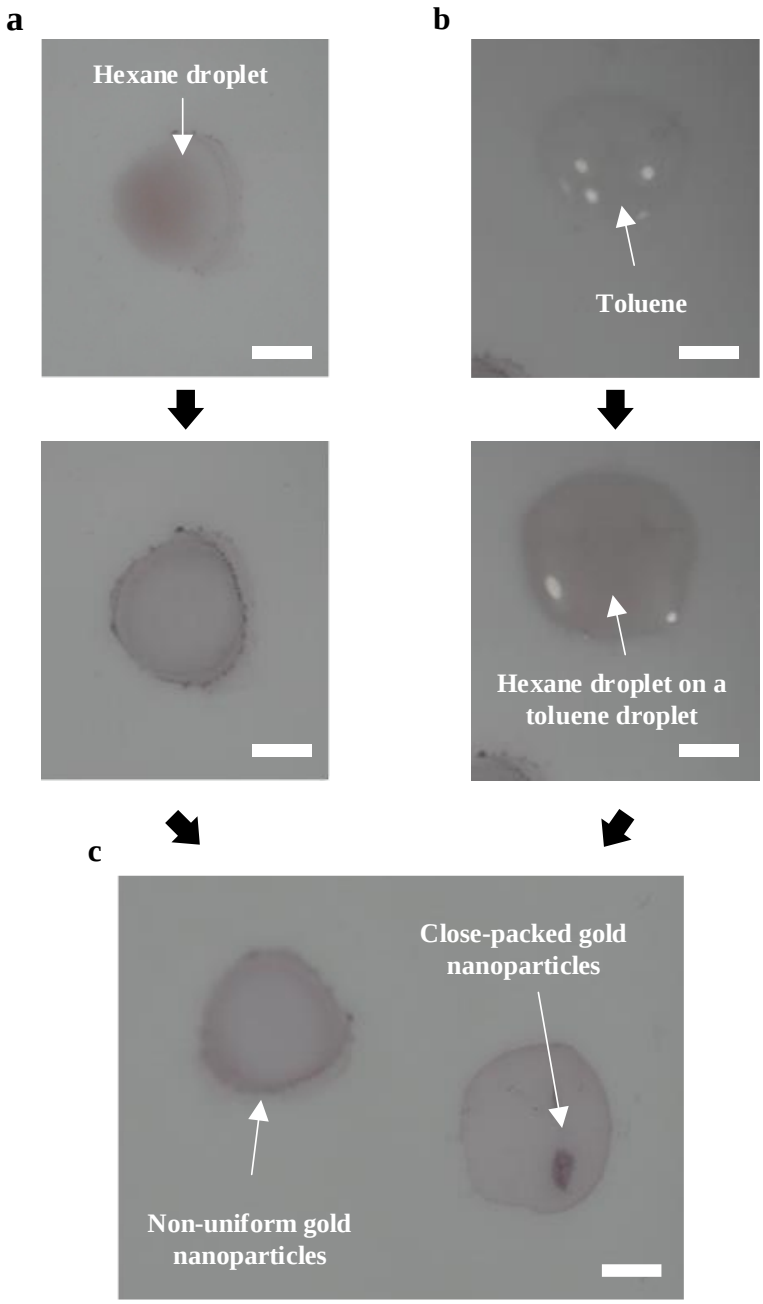

Figure 2-5. 2D self-assembly of gold nanoparticles on a piece of Teflon plate.

(a) A hexane droplet containing gold nanoparticles was directly dropped onto a piece of Teflon plate. Its color remained red throughout the evaporation, implying that gold nanoparticles were kept dispersible within the shrinking hexane droplet. (b) A hexane droplet containing gold nanoparticles was deposited to a larger toluene droplet on a piece of Teflon plate. Mixed with a larger toluene droplet, nanoparticles dispersed in the hexane droplet floated to the air-liquid interface. The interior of the hexane-toluene droplet became colorless immediately and the surface became purple. (c) Monolayer of close-packed nanoparticles was deposited on the substrate after toluene evaporation as opposed to spatially non-uniform gold nanoparticles from just a hexane droplet. Scale bars = 5mm.

3. RESULTS AND DISCUSSION

3.1 Swelling of Millimeter Scale PDMS Pieces in Hexagonal Shape.

A hexagonally shaped PDMS structure was used to measure the volumetric change caused by a nonpolar solvent. After the PDMS samples were immersed in toluene for 3hours, the toluene was absorbed in an uncoated sample, which swelled the PDMS (a) compared to a parylene-coated sample, which was only slightly swollen (b), as shown in Figure 3-1. The non-coated PDMS swelled after immersed in toluene and the lengths between the opposite edges of the PDMS hexagon increased over time, as shown in Figure 3-2. The PDMS began to absorb the solvent and swell rapidly after immersion such that the size of PDMS piece was extended by 1.22 times after one hour. The PDMS piece continuously grew at a relatively slow rate and the PDMS swelling ratio tended to become saturated in a certain range close to 1.3 after 10hours. Finally, the PDMS grew by about 1.29 times in 10hours. Otherwise, the parylene-coated PDMS swelled less in general and extended at most by 1.17 times in 10hours. The swelling ratio of the parylene-coated PDMS for a time of 3hours is important to examine because the PDMS swelled by negligible extent, less than four percent, which means the parylene film prevents the PDMS from swelling effectively during that period. The durability of a parylene film on PDMS for 3hours against toluene enables a parylene-coated PDMS channel to tolerate rapid nanoparticle synthesis when it is completed within an hour.

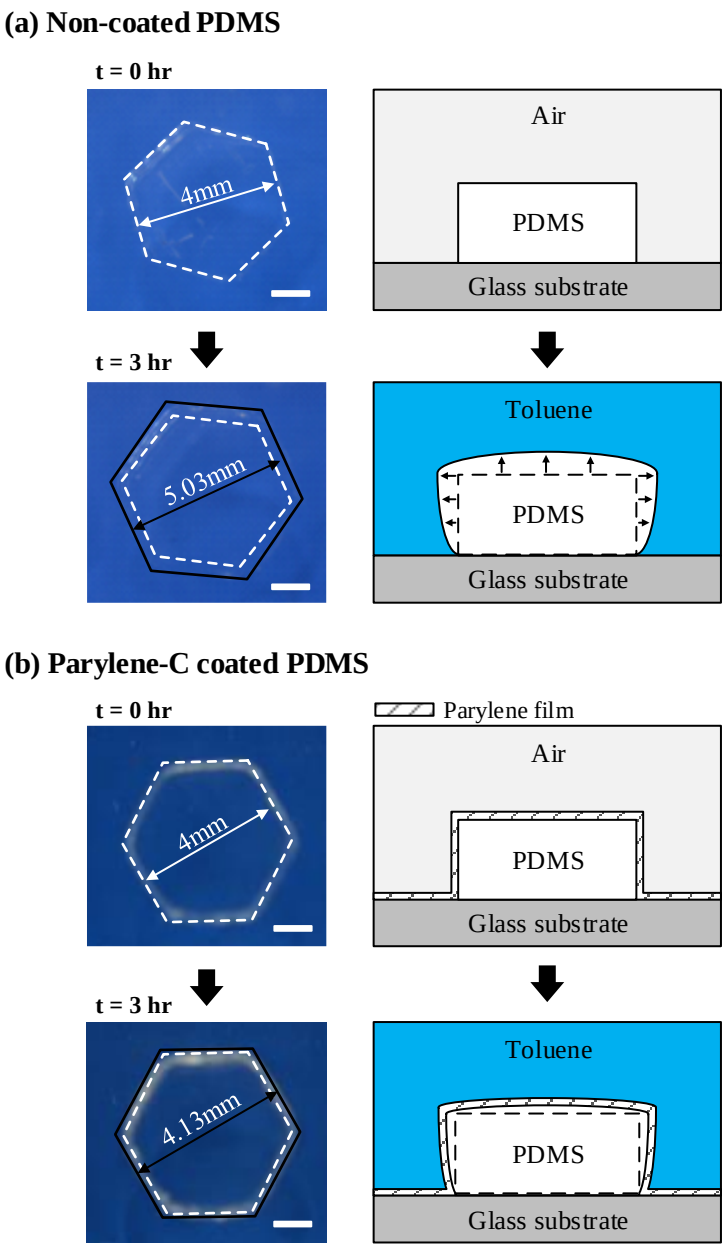

Figure 3-1. Swelling of hexagonal shaped PDMS with or without a parylene coating by toluene

The shape of hexagonal PDMS species were changed by swelling in the nonpolar solvent. Optical images and cross-sectional illustrations of hexagonally shaped PDMS immersed in toluene for 3hours. (a) A hexagonal PDMS species were bonded onto the glass substrate and coated with parylene which has three opening facets and a bounded bottom surface. The porous PDMS swelled in the nonpolar solvent (e.g., toluene). (b) Non-porous parylene film coated onto PDMS was not subjected to swelling for 3hours. Scale bars = 500μm.

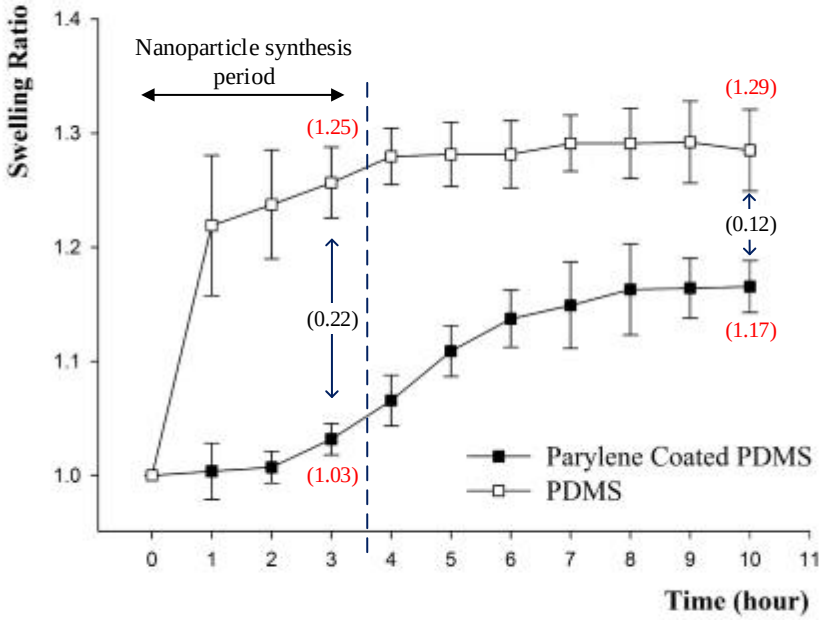

Figure 3-2. Graph of PDMS swelling ratios by toluene for 10hours

The shape of hexagonal PDMS species were changed by swelling in the nonpolar solvent. The lengths between each edges of hexagons were measured and compared to the original lengths to calculate the swelling ratios over time. The swelling ratios of non-coated and parylene-coated PDMS with a hexagonal shape were measured over time for 10hours. The non-coated PDMS swelled in toluene and the lengths between the opposite edges of the hexagon increased continuously over time, becoming extended by 1.29 times in 10 hours. Otherwise, the parylene-coated PDMS less swelled in toluene, swelling by about 1.17 times in 10 hours.

3.2 Swelling of PDMS Microfluidic Channel

We developed a microfluidic setup which was equipped with two syringe pumps integrated with an inverted microscope and imaging devices for a microfluidic system, as shown in Figure 3-3. A simple PDMS microfluidic chip with a straight microchannel and two reservoirs was designed to identify how much nonpolar solvents affect the microchannel wall, as shown in the inset of Figure 3-3. A cross-sectional area of the PDMS channel was decreased and deformed by PDMS swelling while toluene was absorbed in the channel for 3hours, as shown in Figure 3-4a. Because the shape of the channel is unevenly deformed, it is difficult to control the flow rate. In contrast, the parylene-C film coated channel kept its width constant without being deformed by toluene, as shown in Figure 3-4b. Although toluene makes even parylene-coated PDMS swell to some extent after 3hours, the effect of toluene on the inner walls of a PDMS microchannel is much weaker than it is on a millimeter-scale PDMS surface. This indicates that the inner walls of a parylene-coated microchannel scarcely swell due to toluene such that the flow rate is not affected. It was found that a parylene film prevented the solvent from permeating and swelling PDMS and that gaseous monomer permeation into the PDMS channel and conformal coating into the narrow channel were sufficiently achieved. Because a parylene-coated PDMS microfluidic chip is a monolithic device that does not require an additional assembly process compared to a chemically resistant capillary (e.g. Teflon®) assembled device for nanocrystal growth, the parylene-coated PDMS channel is easy to fabricate and apply to nonpolar-solvent-based chemical synthesis applications.

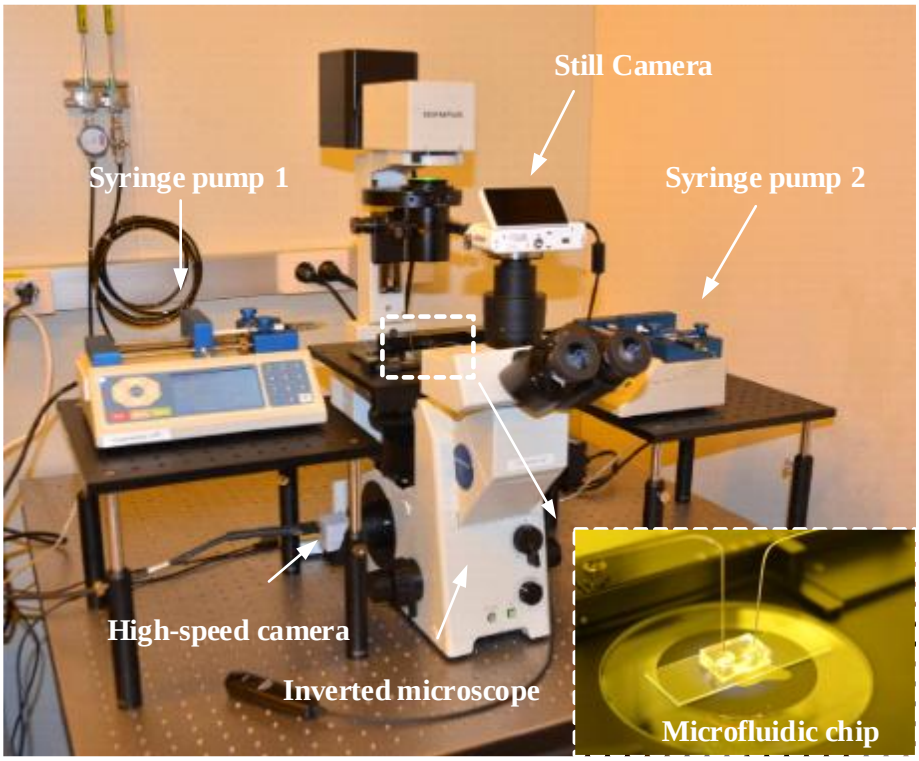

Figure 3-3. Microfluidic system integrated with an inverted microscope and imaging devices

A PDMS microfluidic chip with a straight channel was designed to study the effect of a non-polar solvent on the inner walls in the channel using an integrated microfluidic flow measurement apparatus. (a) Photograph of a microfluidic system equipped with two syringe pumps and integrated with a microscope and imaging devices. The inset shows an optical image of a PDMS microfluidic chip with a straight microchannel. A solvent was dropped onto reservoirs through the long syringe needles and flowed into the straight channel by capillary action.

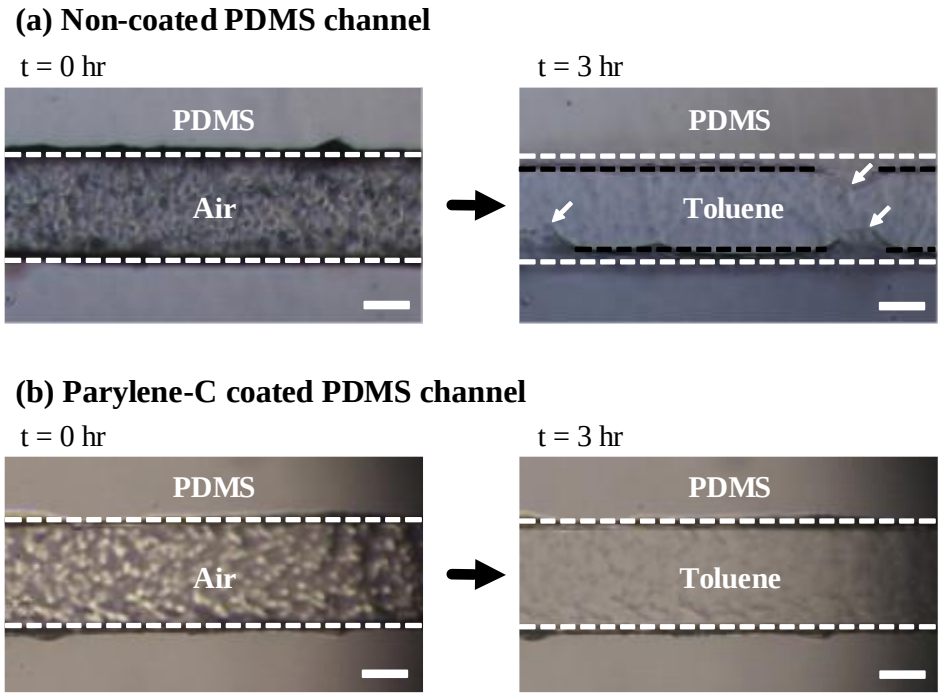

Figure 3-4. Swelling of PDMS microfluidic channel with or without a parylene coating

Optical images of a PDMS straight microchannel to identify the extent to which the nonpolar solvents affect the microchannel wall. (a) Because a non-coated PDMS microchannel was deformed while toluene resided in the channel, the cross-sectional area of the PDMS channel was decreased or deformed by the swelling of the PDMS, as indicated by the white arrows, after three hours. (b) On the other hand, the parylene-coated PDMS channel was decreased to a negligible extent because the parylene film prevents the solvents from permeating into the PDMS over a time of three hours. Scale bars = 100μm

3.3 Droplet based An Air-nonpolar Solvent Interface.

A simply designed PDMS microfluidic channel for droplet generation was fabricated rapidly using a plotter based on a sheet master. We used T-shaped design in which the channel for the injection fluid (DI water or air) is connected perpendicularly to the channel for the carrier fluid (mineral oil or toluene), as shown in Figure 3-5. The widths of the channels for the injection and carrier fluids are 250μm and 500μm, respectively. To test a droplet formation using a fabricated T-shaped microfluidic device, deionized (DI) water and air droplets were generated and carried by mineral oil flowing perpendicularly to the injection channel in the PDMS microfluidic channel as shown in Figure 3-5a-b. In particular, we used toluene as a carrier fluid to generate an air-nonpolar solvent interface, as shown in Figure 3-5c. The droplet-based air-nonpolar solvent interface formed in the channel has the potential to be used to generate a monolayer nanoparticle film on the surfaces of a parylene-coated PDMS channel as demonstrated in 2D self-assemblies of charged gold nanoparticles.

Droplet approach is suitable to test a multiple conditions of chemical synthesis processes which can easily generate an array of droplets composed of different concentration of nanoparticles pre-cursors and solvents. For droplet-based nanocrystal growth, a non-permeable channel surface and two-phase interface is necessary to form an emulsion phase. The suggested T-shaped PDMS microfluidic device generates nonpolar-solvent-based droplets without absorption into the channel surface which is uniformly coated with a parylene film. Our report took a step toward realizing the idea that droplets including nanoparticles and solvents are formed and remain stable in a parylene-coated PDMS channel for an allowable synthesis time, up to 3hours, so that the growth of nanocrystals can be accomplished in the droplets without additional chemically resistant capillary assembly and disassembly processes.

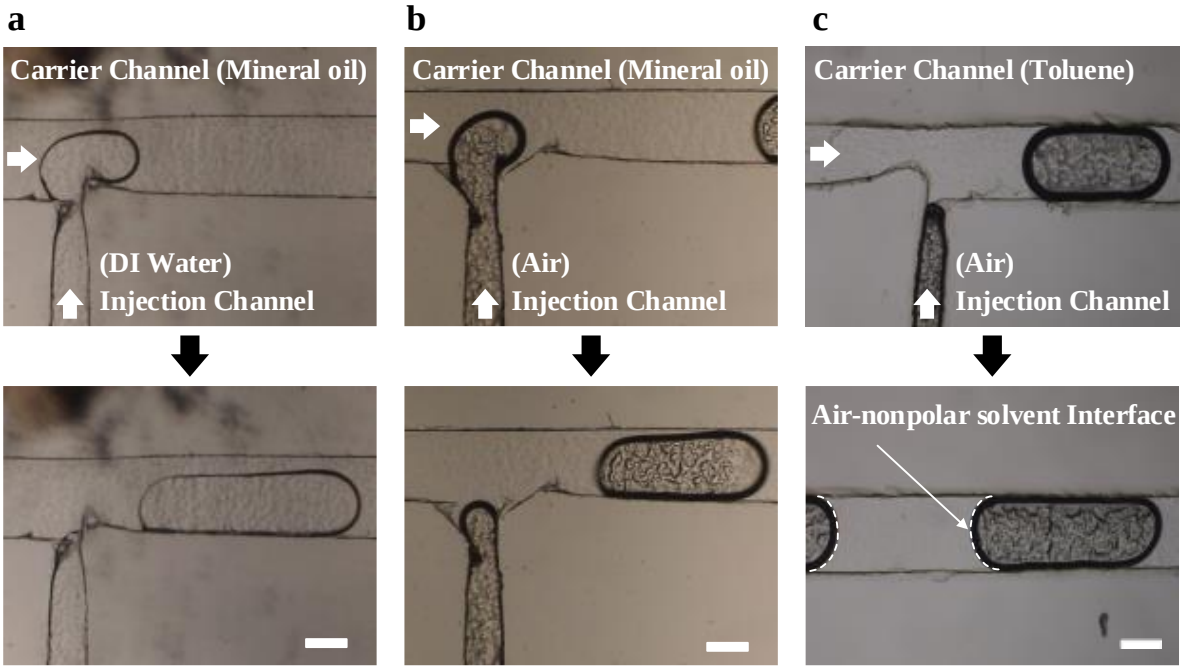

Figure 3-5. Droplet generations and droplet based an air-nonpolar solvent interface

A simply designed PDMS microfluidic channel for droplet generation was fabricated rapidly using a plotter based on a sheet master. The fabricated T-shaped design can generate droplets which has two phase interface, i.e. oil-water, oil-air, and air-nonpolar solvent interfaces. (a) Droplets composed of DI water were generated and carried by mineral oil flowing through the carrier channel with a width of 500μm perpendicular to the DI water channel with a width of 250μm in a T-shaped PDMS microfluidic channel. (b) Air bubbles were also generated in the same way as described above. (c) An air-nonpolar solvent interface was formed by generating air bubbles carried by a toluene flow. Scale bar = 300μm.

4. CONCLUSION

4.1 Conclusion

We determined that the swelling effects of a nonpolar solvent on the inner walls of a PDMS microfluidic channel. Unevenly deformed structure of the channel made it difficult to control the flow rate. Otherwise, a conformal parylene coating inside the PDMS channel sufficiently prevented PDMS surfaces from absorbing nonpolar solvents and swelling. In particular, the durability of a parylene film against nonpolar solvents was retained for approximately 3hours, a period which is long enough for rapid nanoparticle synthesis. In addition, a parylene-coated PDMS microfluidic channel was demonstrated to be useful to form an air-nonpolar solvent interface for the nanoparticles synthesis application by keeping the droplets stable in the microchannel. The parylene-coated PDMS device could enable nonpolar-solvent-based nanocrystals growth in a microfluidic channel and be used in other nonpolar solvent applications as well.

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요 약 문

나노입자 성장을 위한 Poly-p-xylylene 이 코팅된 Poly(dimethylsiloxane) 미세유체 장치

Poly(dimethylsiloxane) (PDMS)로 만들어진 미세유체 장치는 무극성용매가 PDMS 내부에 흡수되어 PDMS 의 부피를 팽창시키는 성질 때문에 무극성용매를 사용하는 화학분야에 적용이 어렵다. 이러한 PDMS 의 흡수와 팽창하는 특성은 PDMS 미세유체 장치의 내부변형과 단면적의 변화를 일으켜서, PDMS 미세유체 장치 내에서의 유체 제어와 용액의 농도 조절을 어렵게 한다. 우리는 무극성용매에 의해 발생하는 PDMS 의 흡수하고 팽창하는 정도를 감소시키기 위해 비다공성 성질을 가진 poly-p-xylylene (parylene)을 증기 화학 증착법으로 코팅한 PDMS 미세유체 장치를 제안한다. Parylene 이 코팅된 PDMS 표면은 무극성용매인 톨루엔 환경내에서 낮은 부피 변화(코팅이 되지 않은 PDMS 의 팽창률 보다 22% 낮음)로 약 3 시간동안 본래의 형태를 유지한다. PDMS 미세 유체 채널 내에 방울 기반의 공기-무극성용매 계면을 발생시킴으로써, poly-p-xylylene 이 코팅된 PDMS 미세 유체 장치가 무극성용매를 사용하는 나노입자 성장 분야에 응용 가능성을 보여준다.

핵심어: Poly(dimethylsioxane), PDMS, 미세유체 장치, Poly-p-xylylene, Parylene, 나노입자 성장