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TiO₂ coated microfluidic devices for recoverable hydrophilic and hydrophobic patterns

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Abstract

We report a simple method for modifying the surfaces of plastic microfluidic devices through dynamic coating process with a nano-colloidal TiO₂ sol. The surface of the thermoplastic, cyclic olefin copolymer (COC) was coated with the TiO₂ film, that displayed an effective photocatalytic property. The hydrophilic surface is obtained in the TiO₂-coated zone of a microfluidic channel, and TiO₂ coated surface degradation can be reversed easily by UV irradiation. The present work shows a photocatalytic activity concerning the effect of TiO₂ coating density, which is controlled by the number of coating cycles. The hydrophilized surface was characterized by the contact angle of water and the TiO₂ coated COC surface reduced the water contact angle from 85° to less than 10° upon UV irradiation. The photocatalytic effect of the layer that was coated five times with TiO₂ was excellent, and the super-hydrophilicity of the TiO₂ surface could be promptly recovered after 10 months of storage at atmospheric conditions. The COC microfluidic devices, in which TiO₂ has been freshly deposited and aged for 10 months, were capable of generating water-in oil-in water (W/O/W) double emulsions easily and uniformly by simple control of the flow rates for demonstration of excellent hydrophilic patterning and recovery of the TiO₂ coated in the microchannels.

Keywords: TiO₂ thin layer, hydrophilic modification, plastic microfluidic device


(Some figures may appear in colour only in the online journal)

1. Introduction

Microfluidic devices can manipulate small amounts of biological/chemical analytes or reagents, usually several nano to femto liters, in the micrometer-sized channels and minimize the analysis time and consumption of reagents. These advantages can be applied effectively to medical diagnostics, drug discovery, and biological and chemical sensing as portable

analytical devices [1]. With increasing interest in portability, mass production, and the fabrication cost of microfluidic devices, several studies have focused on the development of disposable plastic platforms [2–5]. Such plastic microfluidic devices have been fabricated mainly by hot embossing or injection molding. Their wide range of material properties and feasible fabrication methods are especially more beneficial for manufacturing microfluidic chips than silicon or glass with limited optical transparency and complicated bonding process, respectively [6, 7].

The thermoplastic material known as cyclic olefin copolymer (COC) is a useful material for fabricating microfluidic

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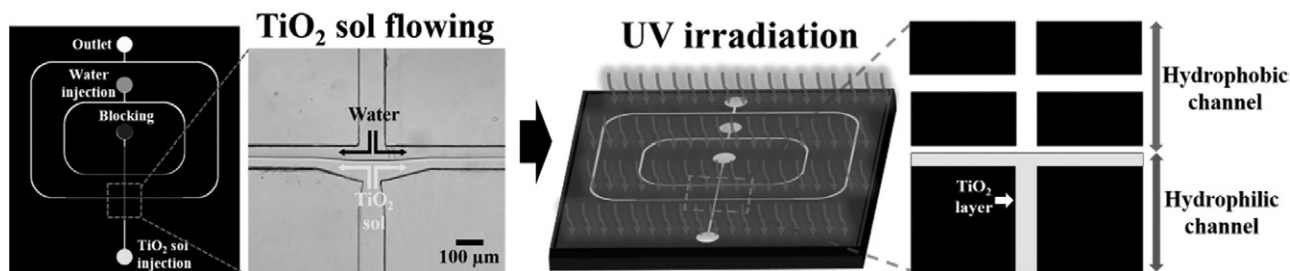


Figure 1. Schematic illustration of hydrophilic coating process using a simple TiO₂ sol flowing in the COC microfluidic channels. (Left) The COC microfluidic device design and an optical image of selective TiO₂ sol dynamic coating using laminar flow for TiO₂ patterning, (Right) UV(A) light irradiation after TiO₂ sol coating procedure; the red box shows the selectively patterned hydrophobic-hydrophilic microchannel zone.

devices due to its high transparency in a wide spectral range, including UV, and its low water absorption and excellent resistance to chemicals [5]. However, like most plastic surfaces, the hydrophobicity of the COC surface must be resolved by chemical modifications for application as biological/chemical microfluidic devices, because hydrophobic adsorption causes loss of the sample, changes in the flow properties, and clogging of the microchannels [6, 8]. Especially, an aqueous solution will not wet the COC surface easily, so it is difficult to control the flow of the aqueous phase in the microchannel [9]. In order to overcome these disadvantages, hydrophilization of COC substrates and microchannels was conducted using dry or wet coating methods, such as plasma treatment [10, 11], polymer grafting [12] and sol-gel process [9, 13]. When the surface of thermoplastic COC is treated with oxygen (O₂) plasma, it becomes hydrophilic due to the OH groups that are generated, but the hydrophobicity was recovered quickly within 10h. This phenomenon could be explained by air contamination or surface rearrangements of the bulk material [14]. The wet-coating methods, such as silanization, photografting of polymer, and the sol-gel process, have been investigated mainly to form a silica-like layer or hydrophilic functional groups to utilize their good and long-lasting hydrophilicity. Most of these coating process treat only three faces of the channel, and then in order to complete the channel they assemble these treated plates and non-coated bare cover plate. The partially modified microchannels can be used in limited applications such as pinning of hydrophilic solution or local addition of functional groups in hydrophilic area [8, 9]. However, the non-treated face may degrade the performance of the microfluidic devices. Specifically in droplet based microfluidic devices, unbalanced shear flow from uneven wetting often fails to generate homogeneous droplets [15, 16]. Dynamic coating process modifies the surface of microchannels as a whole with hydrophilic materials where the functional groups physisorb onto the surface [7, 17, 18]. Among functional materials in dynamic coating, TiO₂ sol can be widely utilized to generate desired surface characteristics such as transparency and homogeneity of the coated layer [19, 20]. Specifically, the TiO₂ surface is biologically and chemically stable and can generate oxygen radicals and hydroxyl groups by UV irradiation [21–24].

In general, the TiO₂ layers prepared by sol-gel process require harsh heat treatment at high temperature (>500 °C)

to achieve high crystallinity that guarantees excellent photocatalytic activity [25]. However, this thermal incompatibility creates a critical challenge in the application of the TiO₂ sol-gel process to various plastic microfluidic platforms. Thus, much effort has been devoted to constructing TiO₂ layers with reasonable photocatalytic activity on plastic substrates through milder heat treatment or even without heat treatment. Park *et al* produced a hydrophilic COC surface upon thorough UV irradiation of the deposited Ti seed layer before the multiple coatings of TiO₂ were applied to enhance the adhesion between the plastic surface and the TiO₂ grains [9]. Yang *et al* presented the photocatalytic activity of a TiO₂ film prepared by a chemically modified, hydrolysis-condensation reaction using titanium alkoxide with acetylacetone for a few, monodispersed, nanometer-sized nanoparticles and reported partial crystallinity of the thin TiO₂ films [25].

In this work, we present a very simple method for hydrophilization of COC microchannels with a thin TiO₂ layer coated by the flow of a colloidal solution. Furthermore, this coating method can easily pattern the hydrophobic and hydrophilic zones using laminar flow of TiO₂ sol and water. Figure 1 shows a schematic diagram of the process. The selectively modified surface (right image of figure 1) is helpful for generating the double emulsion form, which consists of two immiscible phases. Within a microfluidic channel equipped with a stable hydrophilic zone, the dispersed stream is constantly dropped in uniform size by the shearing force of the continuous aqueous phase. Also, the thin layers of TiO₂ coated on the COC substrates have the significant advantage that a hydrophobic transition by aging or mild organic contamination can be recovered easily to a superhydrophilic surface by only UV irradiation. The long-term stability of the photocatalytic conversion by the generation of photo-induced hydroxyl groups was investigated by measuring the water contact angle (WCA).

2. Experiments

2.1. Fabrication of microfluidic chips with a COC

The thermoplastic substrates were COC sheets (TOPAS 5013L-10, Topas Advanced Polymers, Frankfurt, Germany) with a 1mm thickness that were prepared by injection molding. The COC microfluidic devices with microchannels

that measured 100 μm in height and a minimum of 60 μm width were fabricated by the hot embossing method with 200 kPa pressure at 165 $^{\circ}\text{C}$ for 20 min using an electroplated nickel mold. For the electroplating process, the THB-151N negative photoresist (JSR Micro Inc., Sunnyvale, USA) was used for a patterned mold because of its excellent plating tolerance and ease of stripping. Then, the hot-embossed COC plates were drilled to create holes for inlets and outlets of the channels and cleaned for defect-free bonding of the devices. Thermal fusion bonding was used to assemble the device with a pressure of 35 kPa at 145 $^{\circ}\text{C}$. After the bonding process, a polydimethylsiloxane (PDMS) adapter was treated with 5 vol% aminopropyltriethoxysilane (APTES) in deionized (DI) water and then bonded to the inlets of the COC microfluidic devices.

2.2. Deposition of the thin TiO_2 layers on COC surface

To coat the thin TiO_2 layers on the microchannel, a transparent TiO_2 solution was prepared consisting of titanium isopropoxide (Aldrich, 97%), acetylacetone (Junsei, 99%), isopropanol (Aldrich), and DI water. The acetylacetone served as an anti-aggregation agent for the TiO_2 nanoparticles to ensure homogeneous dispersion. The concentration of TiO_2 sol was 0.4 M. Then, an aqueous acid solution (70% nitric acid, HNO_3) was placed into the mixed solution for further hydrolysis. The mixed solution was heated at 80 $^{\circ}\text{C}$ for 12 h, which provided the thermal energy required for the crystallization of the TiO_2 nanoparticles without additional heat treatment after TiO_2 sol coating [25].

The coating process involved either dipping COC plates into the prepared TiO_2 sol or flowing the TiO_2 sol through the microchannels and then rinsing with DI water. To coat the thin TiO_2 layer selectively in the COC channel, as shown in figure 1, the TiO_2 sol and DI water were injected at a flow rate of 100 $\mu\text{l h}^{-1}$ in the channel. The two liquid phases flowed separately at the cross-junction of the COC microchannel at laminar flow. The adsorbed thin TiO_2 layers were dried and cured with UV irradiation to enhance the adhesion strength between the TiO_2 layer and the surface of the COC. The TiO_2 coating process was repeated as described above to achieve a high density of the thin TiO_2 layers. The UV irradiation used to cure the as-deposited TiO_2 layers and achieve the hydrophilic conversion of the surface of the TiO_2 was conducted using a UV light-curing system (Omnigore[®]S2000, Excelitas Technologies Corp., Waltham, USA). The hydrophilicity of the surface was measured using a Phoenix 300 contact angle goniometer (Surface Electro Optics, Inc., Suwon, Korea). The morphology and atomic composition of the COC surface with the TiO_2 layers were investigated by scanning electron microscopy (FE-SEM, Hitachi, Ltd., Tokyo, Japan).

2.3. Formation of the double emulsion

To form the double emulsion, the inner aqueous phase consisted of a 1:1 mixture of Pluronic F68 (Sigma-Aldrich) and DI water. Oleic acid (Fisher Scientific) was used as an oil phase. The external aqueous solution consisted of Pluronic F68 (10%

solution, Sigma-Aldrich) as the surfactant, glycerol (EMD Biosciences Inc., USA), and DI water. Glycerol (20 vol% of the outer aqueous phase) was included in the outer aqueous phase to add viscosity to the continuous phase to enhance the shearing force of the viscous oleic acid. The mixed solutions were contained in 1 ml glass syringes (Gastight 1000 series, Hamilton Company), and the flow rate was controlled with syringe pumps (Ne-100, New Era Pump System, Inc., Wantagh, USA). Each of the solutions for double emulsion formation was injected into the first, second, and third inlets at 110, 130 and 310 $\mu\text{l h}^{-1}$, respectively. An optical microscope (Olympus CKX41) coupled with a high-speed camera (Fastcam Ultima-512, Photron, San Diego, USA) was used to acquire images of the emulsification process.

3. Results and discussion

3.1. Hydrophilic-hydrophobic conversion of the surface of the COC

In order to induce the hydrophilic conversion of the TiO_2 layer formed by dynamic coating in a constructed microfluidic channel, the material of the microfluidic device had to be transparent for irradiation with UV light from outside of the channels, and the COC microfluidic device met this requirement. In addition, the TiO_2 layer that was formed had to be coated uniformly and densely, because the agglomeration of TiO_2 particles was likely to disturb the consistent UV irradiation from outside the microchannel to the TiO_2 coated zone. Prior to the hydrophilic modification of the TiO_2 layer in the COC microchannel, the coating process was performed on a plate substrate due to difficulties associated with obtaining accurate wettability measurements in the microchannels.

To coat the TiO_2 layers uniformly on the COC substrates, the substrates were dipped into the transparent TiO_2 solution and then exposed to UV light, which enhanced the adhesion between the TiO_2 and the COC substrate. The simple coating process was repeated to increase the density of the TiO_2 particles on the surface. After five cycles of the coating process and UV irradiation of 32.4 J cm^{-2} , the WCA of the COC substrate was changed from a hydrophobic surface ($\sim 85^{\circ}$) to a superhydrophilic surface (figures 2(a) and (b)). To evaluate the photocatalytic activity of the TiO_2 layers coated on the COC substrates, the superhydrophilic surface (figure 2(b)) was degraded intentionally to hydrophobic status with tri-chlorosilane vapor. After the vapor deposition, the WCA of the surface was greater than 90 $^{\circ}$. Despite the very thin TiO_2 coating that resulted from the rinsing process for the uniformity of the TiO_2 layer, the hydrophobic surface was switched easily to hydrophilic (A WCA less than 10 $^{\circ}$) upon UV irradiation of 86.4 J cm^{-2} only (figures 2(c) and (d)). This excellent hydrophobic-hydrophilic conversion was achieved through the photocatalytic oxidation reaction of the TiO_2 materials coated on the surface of the COC.

To identify the microstructure of the thin TiO_2 film coated on the COC substrates, the TiO_2 layer resulting from five coating cycles was investigated by a scanning electron microscope (SEM), and the images, including the energy dispersive x-ray spectroscopy (EDS) graph, are presented in figure 3. The

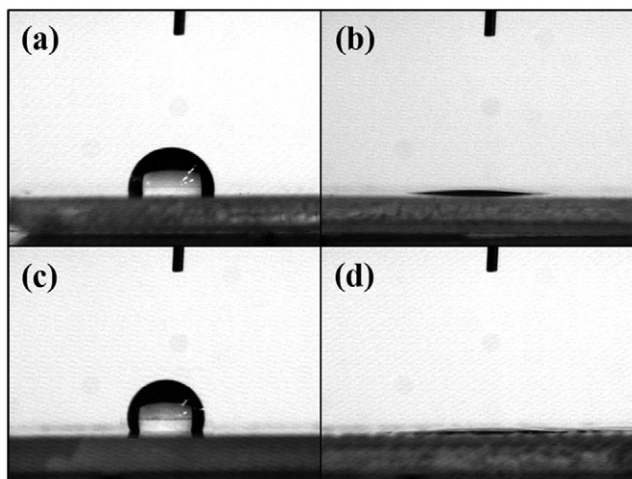


Figure 2. WCA measurement on the COC substrate for hydrophobic-hydrophilic conversion test: (a) bare COC substrate (b) as-coated TiO₂ thin layer on COC (c) trichlorosilane coated COC for hydrophobic surface (d) after UV re-irradiation with trichlorosilane-coated COC substrate.

TiO₂ nanoparticles on the surface of the COC had a homogeneous distribution in size of less than 20 nm with no cracking or aggregation. The uniform distribution could be due to inhibiting the ligand of the acetylacetonate precursor, the acidic condition, and the higher hydrolysis temperature (80 °C) of the TiO₂ sol [25, 26]. Obviously, the two elements of Ti and O are distributed in the thin layer, as revealed by EDS measurements. The completed COC substrate with the thin TiO₂ layer was still transparent. This is important for UV-induced reaction in the channels and optical observation of the micro-channels. We could assume the homogenous distribution of TiO₂ particles in the tens of nanometers size range onto the surface of the COC enabled the high optical transmittance of the substrates [27].

3.2. Photocatalytic activity versus density of TiO₂ nanoparticles

Prior to the hydrophilic modification of the COC micro-channel, the hydrophobic recovery rate and long-term stability of the TiO₂ layers were evaluated to select the optimum coating conditions. Thus, we examined the WCA of TiO₂ layers with varying surface conditions, which were controlled by aging time and coating cycles (one to five times), as shown in figure 4(a). The as-coated TiO₂ layers (0 day) exhibited almost the same WCA of less than 10°. Irrespective of the number of coating cycles, the WCA of the TiO₂-coated surfaces increased rapidly with the period of aging at atmospheric conditions. However, the rate of hydrophobic conversion decreased as the number of coating cycles increased. In two weeks, the WCA of all samples became stabilized around 60°, which is slightly lower than the WCA of intact COC (85°). The hydrophobic conversion of the TiO₂ layers was attributed mainly to the contamination of the surface by the absorption of gaseous organic molecules from the atmosphere [24, 28]. The photocatalytic activity of the TiO₂ layers varied with the aging period, as shown in figure 4(b).

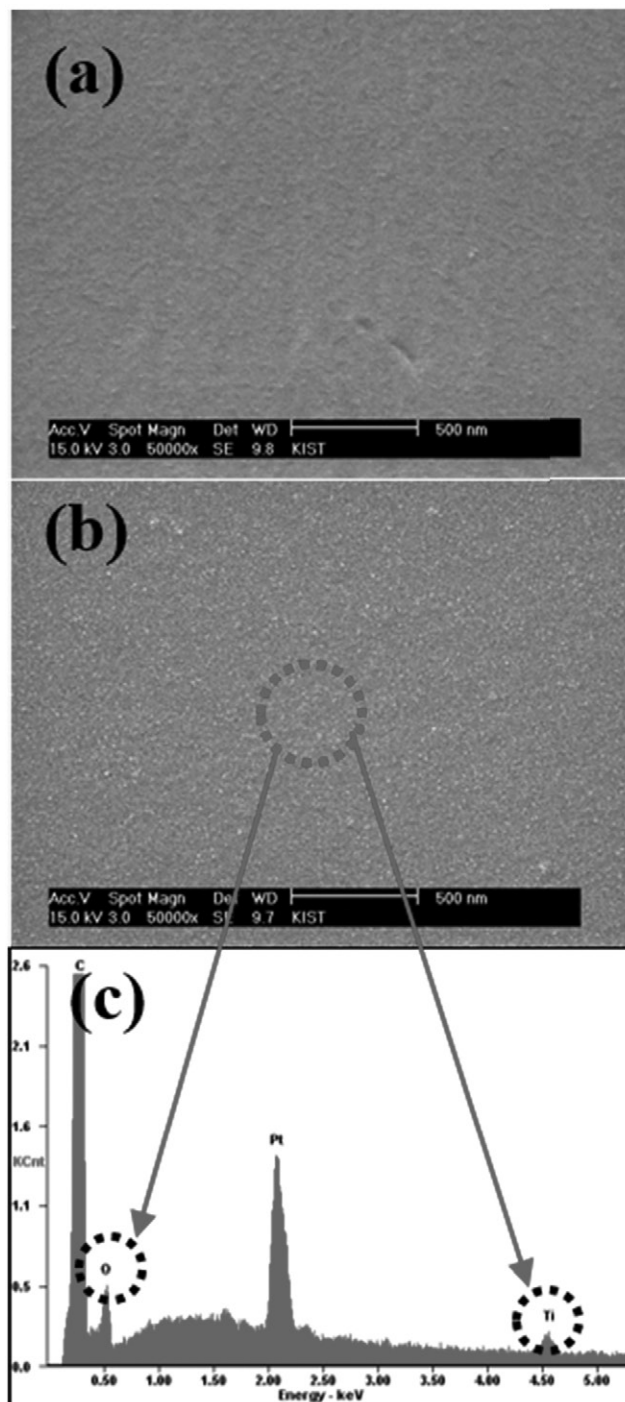


Figure 3. SEM images of the COC substrate: (a) bare COC substrate (b) TiO₂-coated COC with five coatings (c) EDS graph of the as-coated TiO₂ COC substrate.

Each data point represents a WCA of the TiO₂-coated surface after a given aging time and UV irradiation of 32.4 J cm⁻². The surfaces of all of the samples became hydrophilic due to the photocatalytic effect of the TiO₂ surface. The hydrophilic conversion efficiency of the UV-irradiated samples decreased as the storage time increased. However, the coating cycles of 1 to 3 times resulted in increased values of the WCA as the storage time increased irrespective of the UV irradiation. However, in case of coating cycles 4 and 5, the WCA remained around

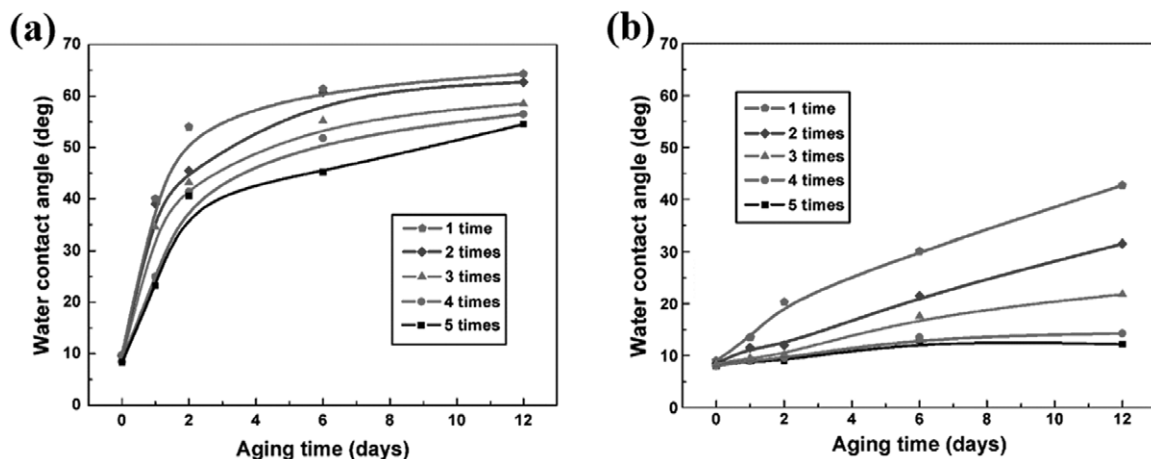


Figure 4. Changes in WCA of multiple TiO₂-coated samples with different storage times: (a) before UV irradiation (b) hydrophilic recovered WCA values after UV irradiation (32.4 J cm⁻²). (All solid line were fitted with plotted data points.)

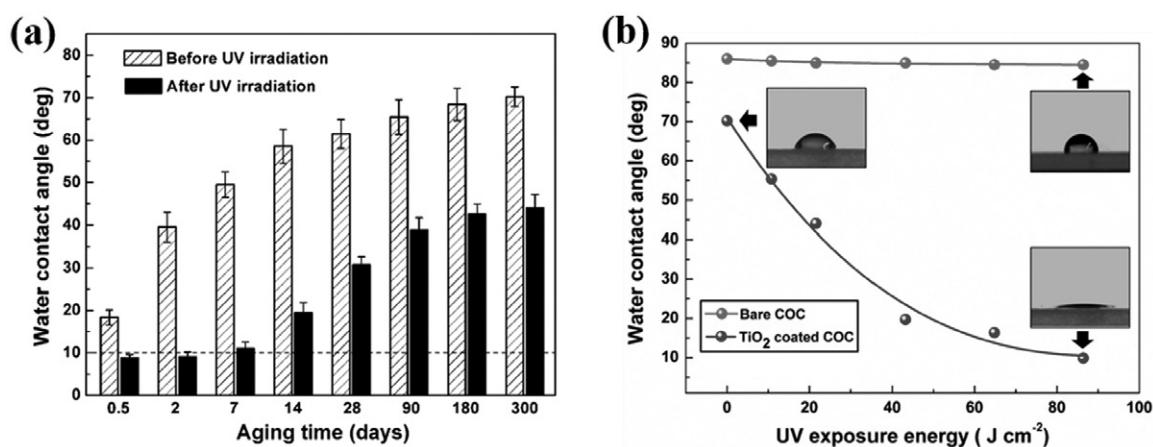


Figure 5. WCA measurement of TiO₂ coated COC substrate for identification of long-term stability: (a) WCA values monitored for 10 months (before UV irradiation) and their WCA values were decreased by UV irradiation energy of 21.6 J cm⁻² (b) different WCA values of TiO₂ layers aged for 10 months and a bare COC with different UV irradiation energies.

10° after 12 days of storage. This result indicated that the amount of photo-induced radicals for the hydrophilic surface depended on the density or surface area of the TiO₂ nanoparticles. For stable photocatalytic activity of the TiO₂ layer, the number of coating cycle was kept at 5 times in the following experiments.

3.3. Long-term stability of TiO₂ thin layers

Thin TiO₂ layers with an anatase structure deposited on silicon or glass substrate are well-known materials with excellent photocatalytic activity [29, 30]. However, their annealing temperature (>500 °C) for crystallization is far above the glass transition temperature (*T_g*) of COC. Thus, the TiO₂ layers coated on the COC substrates were not accessible to the transformation of the crystal structures toward the well-known photocatalytic activity, but its surface retained its strong hydrophilicity, which was in good agreement with previous reports that the amorphous TiO₂ film had stable photocatalytic properties [31]. We presented the photocatalytic activity of the thin TiO₂ layers aged for 12 days in figure 4. Because the long-term stability of the hydrophilic, modified surface is

very important to operate microfluidic devices after a practical storage time, we evaluated the stability of the TiO₂ coated samples for 10 months using WCA measurements. They were kept at room temperature under natural humidity for 10 months and their wettability was monitored with DI water before and after UV irradiation. Before UV irradiation, the TiO₂ coated layers showed rapid hydrophobic conversion within two days, as shown in figure 5(a). When the TiO₂-coated film was stored for more than seven days, the WCA values exceeded 60°, and the WCA for the later days were almost stabilized to 65 ± 5°.

For the UV-exposed samples, the TiO₂ layers that aged within seven days became superhydrophilic, with WCA values less than 10° upon UV irradiation at 21.6 J cm⁻². However, the fixed dose did not recover its superhydrophilicity after two weeks of storage, resulting in a gradual increase in the WCA values as the storage time increased. To examine the influence of UV energy on hydrophilic recovery after long-term storage of the TiO₂, additional doses of irradiation were applied to the TiO₂ film that had aged for 10 months (figure 5(b)). The WCA of the TiO₂-coated films exposed to UV irradiation of less than 21.6 J cm⁻² did not show a significant change due to the lower UV energy. When the UV irradiation energy was greater than

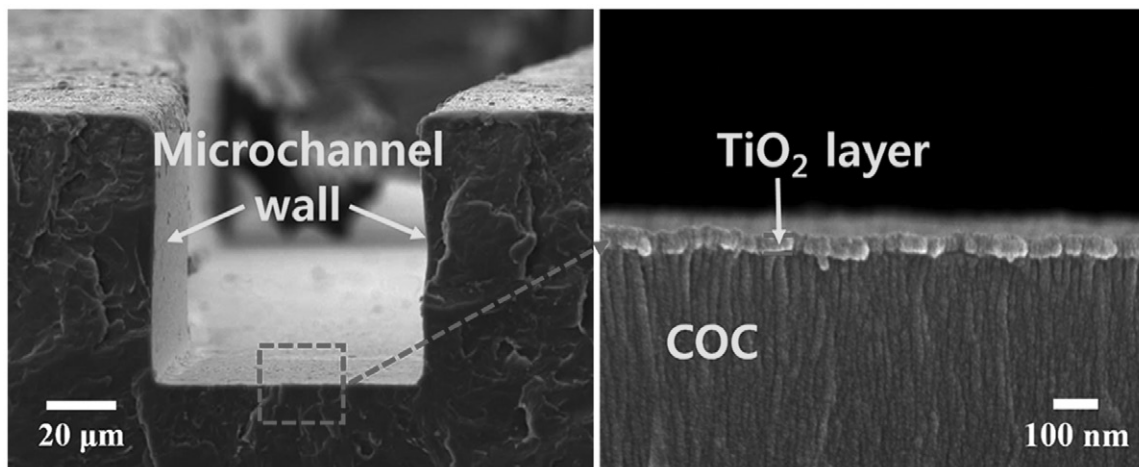


Figure 6. The cross-sectional SEM images of TiO₂-coated microchannel with five coatings: (left) low-magnification image, (right) high-magnification image.

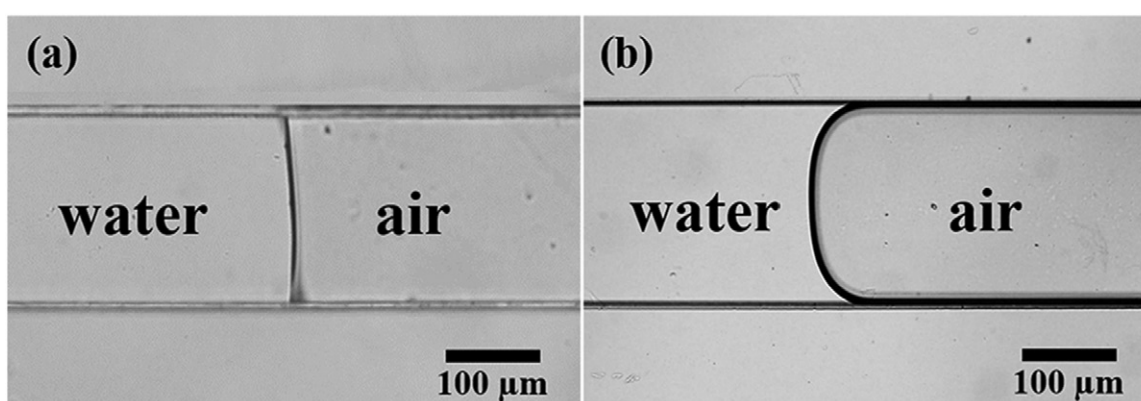


Figure 7. Measurement of the meniscus of water in COC microchannels: (a) bare COC microchannel (b) COC microchannel coated with a layer of TiO₂.

43.2 J cm⁻², the WCA decreased to 10°, which was similar to the WCA of the as-coated TiO₂ layers. However, an intact COC surface did not change the WCA even after UV irradiation of 100 J cm⁻².

Based on these results, the superhydrophilicity of the degraded TiO₂ surface could be easily obtained by UV irradiation. However, the mechanism of the UV-driven hydrophilic phenomenon has yet to be clarified by the experimental results. Possible explanations of the superhydrophilic change have been suggested as follows: (1) photogenerated Ti³⁺ defect sites that are favorable for dissociative water adsorption, thus a new hydroxyl group is generated, which is responsible for the superhydrophilic surface [21, 32] (2) Surface roughness or area of the TiO₂ films can lead to increased hydrophilicity [22, 33].

3.4. Hydrophilic modification and double emulsion formation in COC microchannel

The completed microchannels of COC were coated with TiO₂ film to achieve a uniform, hydrophilic surface as a whole in certain regions of the channel. Instead of the dip-coating process, the channel surface was coated by sequential flow of TiO₂ solution and water. The coating process was repeated for five cycles, as described above. The TiO₂ layer coated on

COC microchannel was investigated by cross-sectional SEM images, as shown in figure 6. The coated TiO₂ layer showed uniform thickness of 55 ± 5 nm and adhered well on COC surface. The uniform thickness could be due to well-synthesized TiO₂ solution with few nanometer-sized TiO₂ molecules and stable water rinsing process. The meniscus of the water in a bare COC microchannel indicated that the surface was hydrophobic (figure 7(a)). As observed in the hydrophilic conversion of COC plates, the hydrophobic surface of bare COC became distinctly hydrophilic in a spatially confined region that was coated with thin TiO₂ layers (figure 7(b)).

To apply the superior hydrophilization of the COC surface with thin TiO₂ layers, we designed a microfluidic system for generating an emulsion, which was capable of high throughput and homogeneous production of multi-functional droplets. In the case of droplet-based microfluidics, the wettability of a microchannel's surface is a crucial parameter in forming an emulsion and, especially, the spatial control of wettability was necessary to form multiple emulsions [18]. In order to make complex dispersed systems, called multiple emulsions, formed by flow-focusing mechanism in the microfluidic devices, its channels require a clear contrast of surface wettability across the cross-junctions. If the microchannel is hydrophobic, water drops in oil are well formed, whereas oil drops in water are

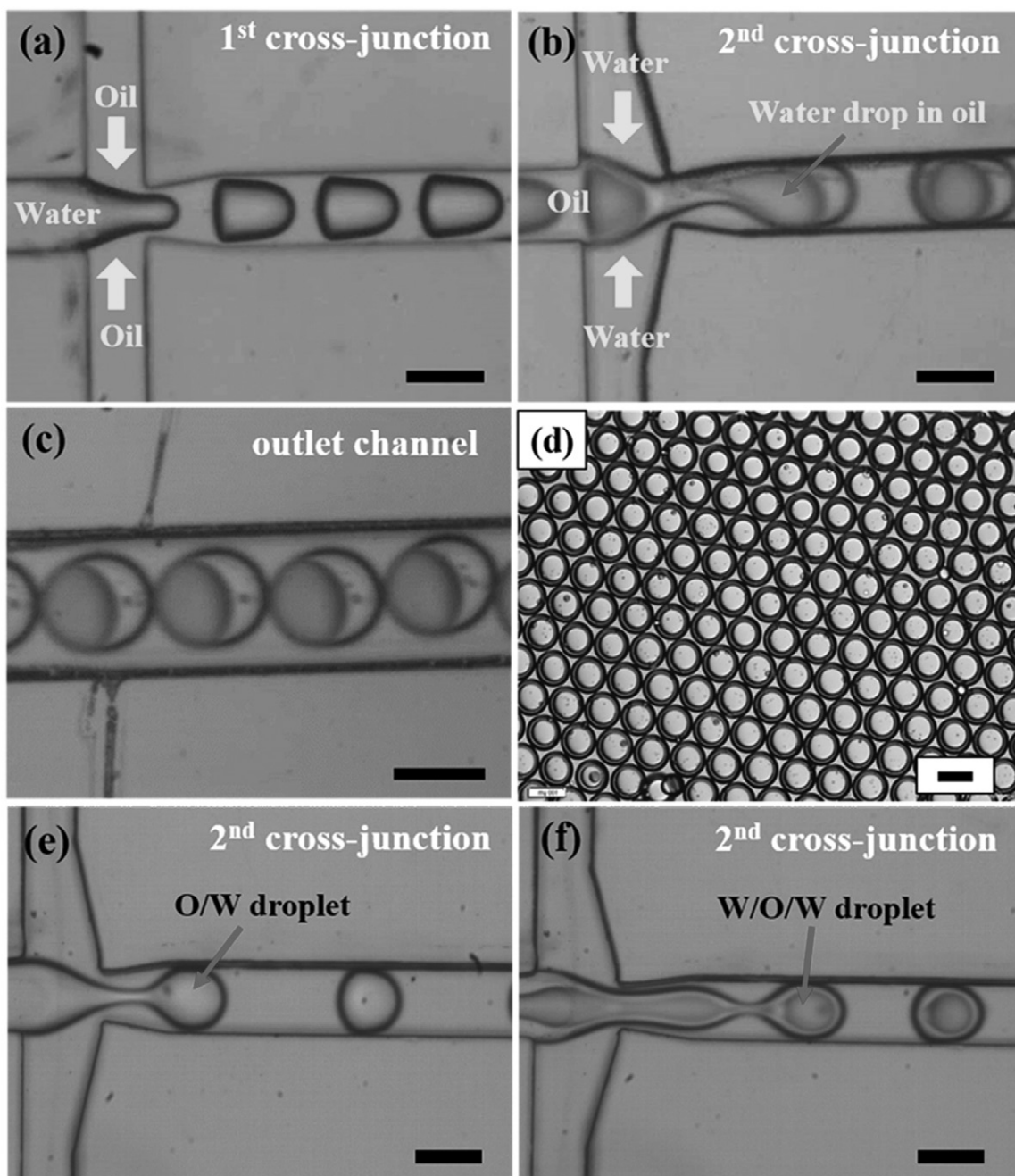


Figure 8. High-throughput production of mono-dispersed emulsions formed by regularized breakup in an as-deposited TiO₂-coated microchannel: (a) W/O single emulsion formation at first cross-junction (b) W/O/W double emulsion formation at second cross-junction (c) as-formed double emulsions flowing to the outlet hole (d) double emulsions collected from outlet hole and long-term stability tests of selective hydrophilic surfaces through formation of single and double emulsions at the second cross-junction for a microfluidic device that was aged for 10 months (e) O/W single emulsion droplets (f) W/O/W double emulsions droplets. The scale bars are 100 μm.

difficult to achieve. On the contrary, the oil drops in the aqueous phase formed easily in the hydrophilic channels. To form water-in oil-in water (W/O/W) double emulsions, the first cross-junction (figure 8(a)) was maintained as a hydrophobic COC surface, and the second cross-junction (figure 8(b)) was modified into a hydrophilic channel. If the surface of second cross-junction channel is not converted to being hydrophilic, the dispersed phase (water drops in oil) is likely to adhere to the side of the microchannel, and no droplets will be formed. After the hydrophilic modification of the second cross-junction by

parallel flow of the TiO₂ solution and water (figure 1), single and double emulsions are formed very homogeneously at the first and second cross-junctions. Especially, the dispersed stream constantly decreased by the shearing force of continuous phase, and the inner oil drops of the double emulsions were encapsulated uniformly, as shown in figure 8(c). The double emulsions that were generated were collected, and they had high mono-dispersity with 110 μm diameters (figure 8(d)). The size of the inner and outer water drops can be controlled by changing the ratio of the flow rates of the dispersed and continuous phases.

To demonstrate that the long-term stability of the hydrophilic patterned microchannel, we also performed the encapsulation of oil drops in water (O/W) and water-in oil drops in water (W/O/W) with aged COC microfluidic devices. The microfluidic devices were kept in air at atmospheric conditions for 10 months and then exposed to UV light at 21.6 J cm^{-2} . After UV irradiation, the single (O/W) and double emulsions (W/O/W) were generated easily with highly mono-dispersed size distributions like the as-prepared microfluidic channels (figures 8(e) and (f)). This result indicated that the COC microfluidic device with the thin TiO_2 layer can provide stable photocatalytic activity after long storage. The simple process, TiO_2 coating and UV irradiation, are applicable to other thermoplastic microfluidic devices because it did not require high-temperature curing or strong organic solvents.

4. Conclusions

In this work, we presented a plastic COC microfluidic device with regional coating of thin hydrophilic TiO_2 layers. The modified hydrophilic surface possesses reasonable photocatalytic activity and long-term stability. Although the superhydrophilicity gradually deteriorated due to the degradation of the photogenerated radicals on surface of the TiO_2 , this deterioration can be reversed by UV irradiation because the TiO_2 has good photocatalytic activity. Furthermore, the hydrophilic-patterned microfluidic device with thin TiO_2 layers is capable of forming mono-dispersed double emulsions, which can be generated by the contrast of surface wettability at the cross-junctions of the microchannels. The thin TiO_2 layers in the COC microchannels can recover outstanding hydrophilicity after 10 months, which was demonstrated by the stable and uniform formation of oil-in water (O/W) and water-in oil-in water (W/O/W) emulsions. For mass production of functional microfluidic chips, the proposed fabrication protocol is superior in reliability to various existing hydrophilic modification methods in thermoplastic microchannels. The facile recovery of the hydrophilicity of the thin TiO_2 layer can be used in the development of plastic microfluidic devices.

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