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Convenient Method for Modifying Poly(dimethylsiloxane) To Be Airtight and Resistive against Absorption of Small Molecules

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In this paper we present a simple and rapid method of modifying poly(dimethylsiloxane) (PDMS) surfaces with paraffin wax. PDMS that contains a layer of paraffin wax at its surface resists the absorption of hydrophobic molecules; we used fluorescence microscopy to confirm that paraffin-modified PDMS resists the absorption of rhodamine B. Furthermore, we demonstrated that microfluidic devices made from PDMS that contains a surface layer of paraffin wax prevent efficiently the transport of gas molecules through the bulk and into microchannels. We characterized the surface of PDMS that contains paraffin wax using the water contact angle, optical transmission, and X-ray photoelectron spectroscopy. We show that PDMS that contains paraffin wax can be substituted for native PDMS; specifically, we fabricated peristaltic valves in PDMS that contains paraffin wax, and the valves showed no degradation in performance after multiple open/close cycles. Finally, we show how to use PDMS that has been treated with paraffin wax as a mold for the fabrication of PDMS replicas; this approach avoids silanization of PDMS, which is a time-consuming step in soft lithography. The wax-modified PDMS channels also show performance superiro to that of bare PDMS in micellar electrokinetic chromatography for quantitative analysis.

Microfluidic devices that are made from polymers are cheaper than the same devices made from silicon or glass. Poly(dimethylsiloxane) (PDMS) is one of the most popular choices among researchers to fabricate polymer microfluidic devices;[1−7] however, in certain applications in biochemistry and bioanalysis,[8] the use of PDMS presents several challenges.[9] Microfluidic devices made from PDMS absorb small molecules from the solutions that flow through channels, which fouls the channel and complicates quantitative analysis of the solution phase.[10−14] The gas permeability of PDMS can also be problematic: the evaporation of water molecules through the walls of a PDMS microchannel changes the concentration of analytes in the microchannels.[15] Other polymers that are used to fabricate microfluidic devices, e.g., PMMA and TPE,[16] do not have these problems; however, the fabrication of devices using these polymers is more complicated, and the devices are significantly more rigid than PDMS devices, which limits their utility as microfluidic valves.

Two methods are available that modify PDMS and limit its absorption of small molecules. The first is to modify the bulk or surface of PDMS with other materials. For example, Culbertson et al. demonstrated that modification of PDMS by SiO_2 nanoparticles reduces the absorption by PDMS of small molecules;[17] however, the modified PDMS−SiO_2 was harder than unmodified PDMS, and small molecules adsorbed to the channel surface. Also, the silica layer can crack and therefore fail to block the absorption. Sol−gel modification of the PDMS microchannel using titania, vanadia, or zirconia was also reported using an "inside out" approach, where the metal alkoxide precursor flows through the channels and diffuses into the sidewalls.[18] Coating PDMS with Teflon or glass[19,20] limits the utility of the resulting composite material as microfluidic valves. Takayama and colleagues demonstrated that transport of gas molecules through PDMS can be avoided by using a PDMS−Parylene−PDMS hybrid membrane,[15] but the fabrication is complicated and is not easy to adapt to other channel structures.

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10.1021/ac100830t © 2010 American Chemical Society
Published on Web 06/21/2010

The second method that limits the absorption by PDMS of small molecules modifies directly the PDMS polymer, e.g., a perfluorinated PDMS. DeSimone's group and Quake's group have synthesized silicones of photocurable perfluoropolyethers (PFPEs), which are elastomeric and inert to most solvents,[21] but still permeable to gases; this material is not commercially available, so wide use of this material is difficult to envisage presently.

In this paper, we introduce a convenient method that modifies PDMS with paraffin wax; the result is a composite material that limits the absorption of small molecules from entering the PDMS bulk and that limits the diffusion of gas molecules through PDMS into microfluidic channels. Paraffin wax is used as a cheap and stable material to make airtight and hydrophobic seals. When melted at high temperature, paraffin can diffuse into the bulk of PDMS; when the temperature is reduced to room temperature, the paraffin wax in PDMS is less mobile. This layer of wax in PDMS resists the absorption of small molecules from aqueous solution. The modification process takes ~1 min using a conventional laboratory hot plate. We optimized the conditions for modifying both open PDMS channels and sealed PDMS channels using paraffin wax. We used rhodamine B dye molecules and fluorescence microscopy to determine the ability of PDMS that contains paraffin wax to resist the absorption of small molecules; the results show significant improvement compared with unmodified PDMS. We used ammonia gas and a pH-sensitive fluorescent dye to observe the efficiency of PDMS that contains paraffin to reduce transport of gas molecules through PDMS and into microchannels. We fabricated peristaltic valves using PDMS that contains paraffin wax; the low modulus of wax enables the valves to perform well for hundreds of close/open cycles. In addition, we demonstrated that PDMS that contains paraffin wax can be used as a master for molding replicas using PDMS (which does not contain paraffin wax); this method is simpler and faster than the conventional method that requires fluorinating the surface of the PDMS master overnight. We believe that the convenience of our method makes it attractive and useful to researchers in the fields of microfluidics and soft lithography.

EXPERIMENTAL SECTION

Materials and Equipment. We obtained PDMS prepolymer from GE Silicones RTV615 (GE). We purchased paraffin wax from Aldrich. We obtained ammonia solution and acetic acid from Shanghai Chemical Reagents Corp. (Shanghai, China). We purchased fluorescein (sodium salt), rhodamine B, rhodamine 6G, and other chemicals from Aldrich. All reagents were of analytical grade and used without further purification.

X-ray photoelectron spectroscopy (XPS) was performed using a model PHI 5600 (peak positions normalized to the carbon peak at 285 eV). Contact angles were measured with a JC2000A contact angle analyzer (Zhongchen Digital Technology and Equipment, Shanghai, China) at room temperature. We used a fluorescence microscope (AZ100, Nikon, Japan) and a digital camera (DS-Fi1, Nikon, Japan) to observe all fluorescent samples. Fluorescent images of rhodamine B, rhodamine 6G, and sodium fluorescein were collected with a red filter (excitation, 540−580 nm; emission, 600−640 nm) and a green filter (excitation, 460−490 nm; emission, 515−555 nm).

Fabrication of the PDMS Microchip. Chip fabrication was adapted from procedures previously reported.[22] We mixed thoroughly PDMS prepolymers A and B (10:1, w/w), and we poured the mixture over SU-8 masters (SU-8 2050, Microchem, prepared using photolithography at the Nanofabrication Facility, The Hong Kong University of Science and Technology). After degassing the mixture, we cured the PDMS (80 °C, 2 h). The cured PDMS was peeled from the master, and holes were punched as reservoirs. Flat PDMS pieces were obtained by casting the prepolymer mixture on clean wafers. Cured PDMS pieces were sealed after plasma treatment and baked (80 °C, 30 min) to form enclosed chips.

Modification of the PDMS. *Modification of the PDMS Channel.* We fabricated PDMS channels that were 100 μm wide and ~50 μm deep. Prior to modifying the PDMS with paraffin wax, we heated the PDMS chip and wax (100 °C) using a hot plate. We filled the microchannels in PDMS with melted paraffin wax using a pipet and removed the wax after 1 min. We left the chip to cool to room temperature.

Modification of the PDMS Surface. We placed several glass slides on a hot plate (Dataplate 732, OMC); we placed a piece of Kimwipes paper (Kimberly-Clark, GA, Canada) on top of each of them. The hot plate was set to 100 °C unless stated otherwise. We dropped melted paraffin wax onto the papers until the papers were soaked with paraffin wax; we put PDMS plates on top of the papers. We removed each stack (glass/paper soaked in wax/PDMS) from the hot plate and allowed them to cool to room temperature.

Making the PDMS Replica from the PDMS Mold. The PDMS used as a "master" was molded from an SU-8 "premaster", which contained a negative relief of 200 μm diameter and ~50 μm deep holes, so that the obtained PDMS master had a positive relief of 200 μm diameter and ~50 μm tall columns. The PDMS master was modified with paraffin wax (100 °C, 1 min) following the method described in the section "Modification of the PDMS". After modification, we cast PDMS prepolymer onto the mold, and we cured the prepolymer in an oven (80 °C, 1 h). We peeled the PDMS replica from the PDMS mold.

RESULTS AND DISCUSSION

Modification of the PDMS Using Paraffin. Paraffin wax is an alkane hydrocarbon that contains at least 20 carbon atoms. It is known that PDMS swells in contact with liquid alkanes.[10] We propose that paraffin wax, when heated and in contact with PDMS, diffuses into and swells PDMS; however, because of its relatively large molecular weight, the diffusion is slow, which limits the extent of diffusion by paraffin wax into PDMS. The paraffin wax, when cooled to room temperature, is less mobile and, for the purposes of our experiments, becomes a barrier at the surface of the PDMS.

The modification method reported here is less expensive and more convenient than conventional silanization methods. Typically, the process requires less than 5 min. We used paper tissue as a reservoir for paraffin wax, which restricted the flow of the wax to the boundaries of the tissue and could be used to modify several tens of PDMS substrates. We used an adhesive tape to remove

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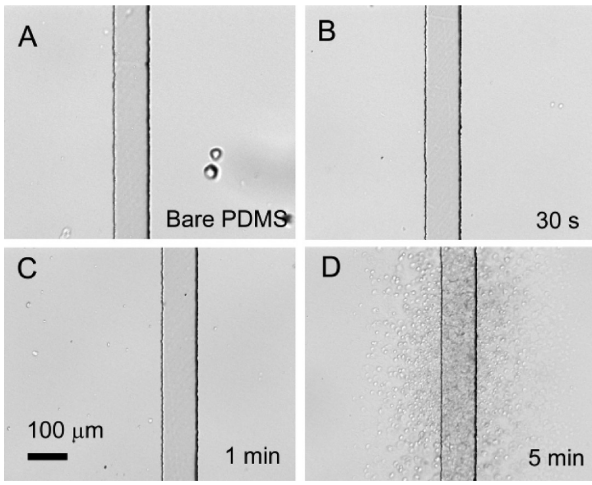

Figure 1. Optical micrographs of PDMS channels that were modified by paraffin wax (100 °C): (A) bare PDMS; (B−D) PDMS channels that were modified for 30 s, 1 min, and 5 min. The photos were taken immediately after the time indicated for modification.

excess wax from the surface of PDMS, but this was not required in most cases.

Paraffin wax that modifies the surfaces of sealed microfluidic channels could be removed quickly from the channel by flowing air through the microchannel (when the wax was molten). Figure 1 shows images of PDMS microchannels that are modified by paraffin wax. Microchannels that are modified by paraffin wax are indistinguishable from microchannels that are unmodified when the modification process occurs within a minute (Figure 1B,C); longer modification times cause aggregates of paraffin wax to form along the microchannel (Figure 1D).

Small Molecule Resistance. We determined the ability of PDMS microchannels that are modified by paraffin wax to resist the absorption of small molecules from the liquid flowing in the microchannels. Figure 2 shows the results of a comparative study between PDMS microchannels that are modified by paraffin wax and unmodified PDMS microchannels. There is significant absorption of rhodamine B from the aqueous phase by unmodified PDMS microchannels, which is consistent with literature reports;[17] however, the absorption of rhodamine B by PDMS microchannels modified by paraffin wax is negligible. In the case of PDMS microchannels that are modified by paraffin wax, the profile of the fluorescence intensity across the width of the channel matches closely the actual physical geometry of the microchannel; this is a significant improvement over other recent efforts to limit the absorption of small molecules by PDMS,[17,20] in which there was a strong adsorption on the modified PDMS surface. The ability of PDMS microchannels that are modified by paraffin wax to limit the absorption as well as adsorption of small molecules enables their application to quantitative diagnostic assays and clinical applications.

We investigated whether PDMS that is modified with paraffin wax can be used to fabricate useful microfluidic devices. We fabricated a microfluidic device that integrates a peristaltic microvalve[23,24] into microchannels (Figure 3). The microfluidic device was modified by paraffin wax using the methods described earlier; we flowed an aqueous solution of rhodamine B into the microchannels, and we performed 1000 open/close cycles using the valve. We washed the microchannels using deionized water, and we could not distinguish using fluorescence microscopy the regions of the microchannel that contained valves from the regions that did not; this is evidence that absorption of rhodamine B by PDMS that is modified by paraffin wax does not increase as a result of using the valve. This is a simple demonstration that illustrates how our composite material can be applied to functional microfluidic devices.

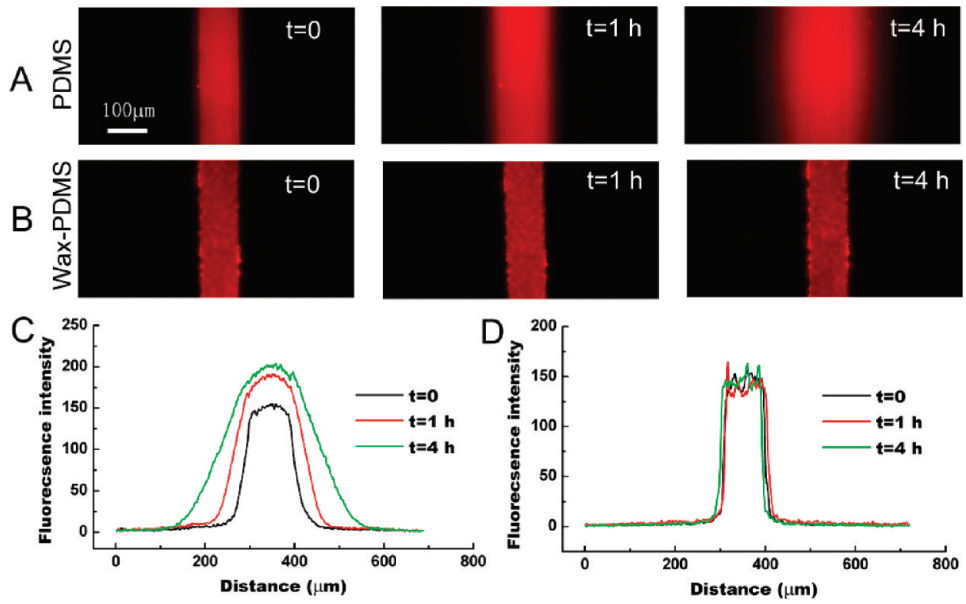

Figure 2. Fluorescent images and fluorescence intensity profiles of PDMS channels filled with rhodamine B. The channels were all 15 mm in length, 100 μm in width, and 50 μm in height. (A) Fluorescent image of the bare PDMS channel. (B) Fluorescent image of the modified (100 °C, 1 min) PDMS channel. (C) Fluorescence intensity profile across the bare PDMS channel. (D) Fluorescence intensity profile across the modified PDMS channel. The modified channel resisted the absorption of rhodamine B: after 1 h the fluorescent profile of the channel wall was still distinct. In comparison, the fluorescence intensity profile of the bare PDMS channel blurred quickly: the fluorescent dye defused several hundreds of micrometers after only a few minutes, indicating significant absorption of rhodamine B.

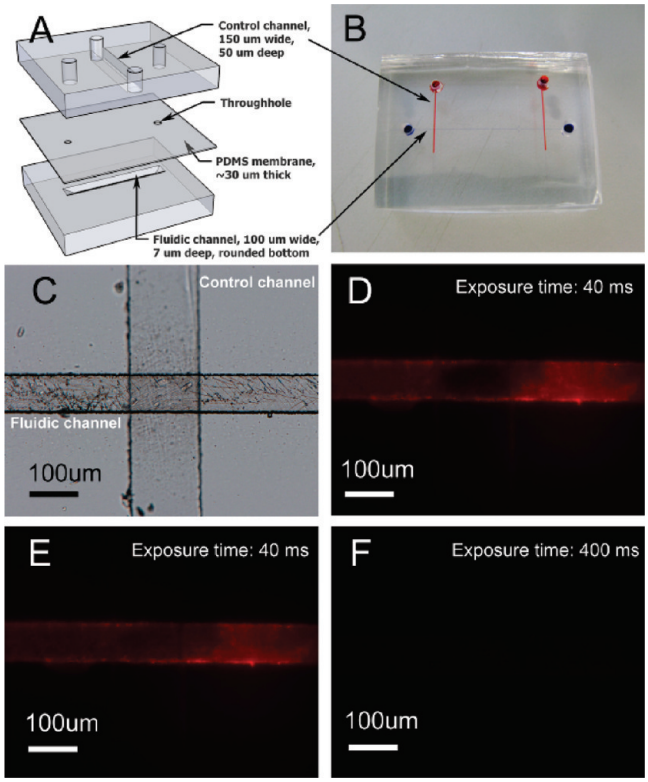

Figure 3. Pneumatic valves in PDMS that was modified with paraffin wax. (A) Schematic illustration of the construction of the PDMS chip with an integrated valve. We constructed the chip by sealing two layers of PDMS channels with a ~30 μm thick PDMS membrane between them. The top layer, which contains control channels, was cast with an SU-8 mold. The bottom layer channel, as the fluidic channel, was fabricated with a reflowed AZ4620 mold. Prior to use, this microchannel was modified with paraffin wax (100 °C, 1 min). (B) Optical micrograph of the microchip. The microchannel was filled with blue ink, and the control channel was filled with red ink. (C) Wide-field picture that shows the valve at the intersection of both microchannels. (D, E) Fluorescent image taken at the valve area when the membrane was pressed and released, respectively. (F) Fluorescent image of the valve area after operation of the valve 1000 times and rinsing of the channel with DI water for 1 min.

Gas Permeability. We investigated the permeability of PDMS that is modified by paraffin wax to gas (Figure 4). We fabricated two microchannels in PDMS, and we modified one microchannel with paraffin wax (top layer); we sealed these channels to another piece of PDMS that contained a microchannel that was orthogonal to and in-plane with the first two microchannels (bottom layer). We flowed an acidic solution of sodium fluorescein in each of the microchannels in the top layer and a solution of ammonia in the microchannel in the bottom layer. Sodium fluorescein fluoresces poorly in acidic media, so diffusion of ammonia into the microchannels in the top layer would increase the fluorescence intensity observed in those microchannels. For similar exposure times we recorded negligible fluorescence intensity from the microchannel in the top layer that was modified by paraffin wax (over the course of 10 min of observation); however, we observed fluorescence in the microchannel in the top layer that was not modified. We carried out an additional experiment to identify the difference in air permeability of modified and unmodified PDMS by infusing blue ink into microchannels that were sealed at one end (dead-end channels),[25] in which the unmodified PDMS channel was quickly filled with blue ink while the modified one was not filled even after a few hours (Figure S1, Supporting Information). We propose that PDMS microchannels modified by paraffin wax can be used as airtight microchannels in microfluidic devices.

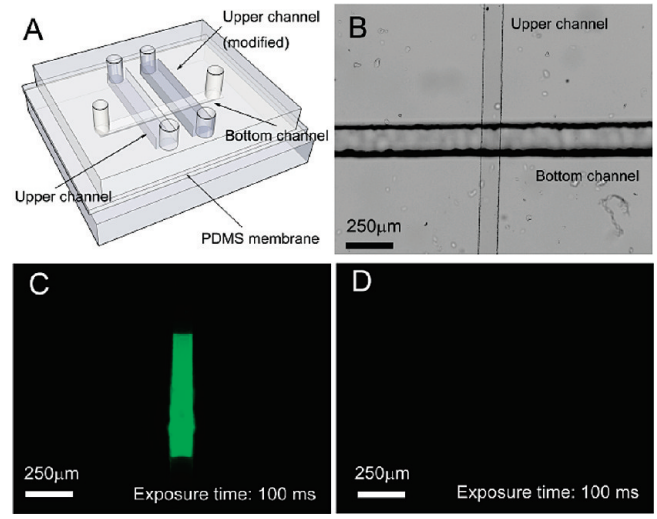

Figure 4. PDMS modified with paraffin wax does not transport gas across its interface. (A) Scheme of the chip design for the gas permeability test. We sealed a 50 μm thick PDMS membrane between two pieces of PDMS with features on them to make a sandwich chip. We modified one of the two channels in the top layer with paraffin at 100 °C for 1 min (gray); the other microchannel was not modified. Prior to use, we filled the top channels with a solution of 10 mM sodium fluorescein (pH tuned to 4.0 with acetic acid). (B) Intersection area of the bare PDMS channel and the bottom channel. (C, D) Fluorescent images of the bare PDMS channel and the paraffin-modified channel, respectively, taken at the intersections of the channels 20 s after infusion of 35% (w/w) ammonia solution into the bottom channel.

Investigation of Wax Modification Parameters. We demonstrated that PDMS that is modified with paraffin wax prevents efficiently the absorption of small molecules by PDMS. We placed a drop of a solution of a fluorescent dye (rhodamine B) onto a modified PDMS surface for several minutes and rinsed the surface using deionized water. We performed a similar experiment using unmodified PDMS and compared both results (Figure 5). We used fluorescence to detect the presence of physisorbed dye at the surfaces of modified and unmodified PDMS; the results show an almost 3 log reduction in the amount of dye absorbed by PDMS (or adsorbed on its surface) that was modified with paraffin wax compared with the result from unmodified PDMS.

Figure 6A shows the relationship between the duration and temperature of the process that modifies PDMS with paraffin wax and the fluorescent signal from physisorbed rhodamine B, which measures how efficiently the modified PDMS resists the absorption of small molecules. The data confirm that PDMS modified with paraffin wax resists the absorption of small molecules.

Figure 6B presents the optical absorbance of PDMS that is modified with paraffin wax as a function of temperature and exposure time to paraffin wax. An increase in temperature or

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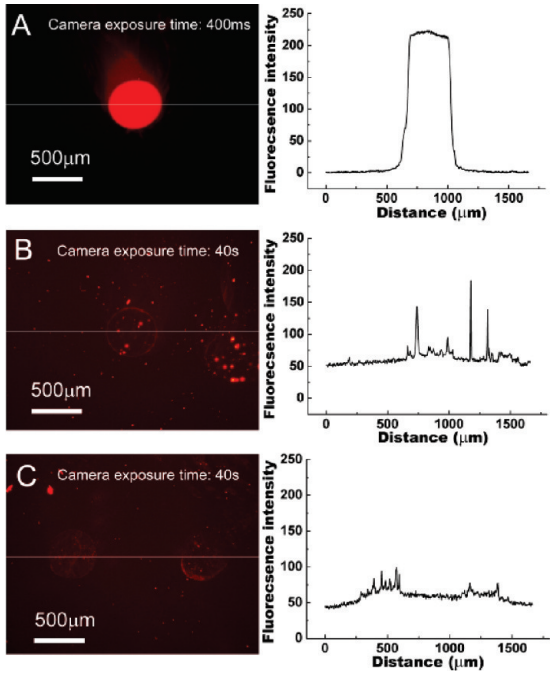

Figure 5. Fluorescent images and intensity profiles of the absorbed rhodamine B on the surface of PDMS. A drop of 0.1 mM rhodamine B solution was applied to the surface of PDMS and washed away with DI water after 3 min, and fluorescent images were recorded immediately. Corresponding fluorescence intensity profiles across the spots (dashed lines) are shown to the right of the pictures. (A) Bare PDMS. The exposure time for taking the photo was 400 ms. (B) Modified PDMS (120 °C, 5 min). (C) Modified PDMS which has been bent. The PDMS slab was modified with paraffin wax (120 °C, 30 s) and then folded in half. We used two drops of rhodamine B to demonstrate the integrity of the modification after the PDMS was unfolded.

exposure time to paraffin wax increases the absorbance of the PDMS. The measured absorbance ranged from 0.1 (80 °C, 1 min) to 1.2 (110 °C, 5 min), which indicates that shorter exposure times to wax permit optical absorbance measurements, but longer exposure times do not. Short exposure times are, however, sufficient to produce PDMS surfaces that resist efficiently the absorption of small molecules. We normally modify PDMS with wax at 100 °C for 1 min because this modification can lower the dye absorption by 2 orders of magnitude and keep the material highly transparent (the naked eye cannot tell the difference in 1 mm thick PDMS pieces that are untreated and wax-treated). Modifications with a higher temperature and a longer time start to turn PDMS cloudy and finally opaque.

We used XPS to characterize the surfaces of PDMS that are modified with paraffin wax (Figure 6C). The concentration of silicon and oxygen decreased significantly and the concentration of carbon increased, which implies that most of the surface consisted of paraffin. However, silicon peaks are still there even after a longer treatment time, which is evidence of wax being in PDMS but not covering the PDMS surface.

To characterize the change in wettability after modification, the advancing contact angles of water on the modified PDMS surface were measured (Figure 6D). It can be observed that the wax modification increased the contact angle, indicating an enhancement of the hydrophobicity of the surface. The hydrophobicity increased with exposure time to paraffin wax and with temperature and finally reached a stable contact angle of about 130°. The contact angle of 130° was greater than the result reported from a newly prepared "smooth" surface with similar paraffin, but is consistent with "rougher" surfaces,[26] which implies

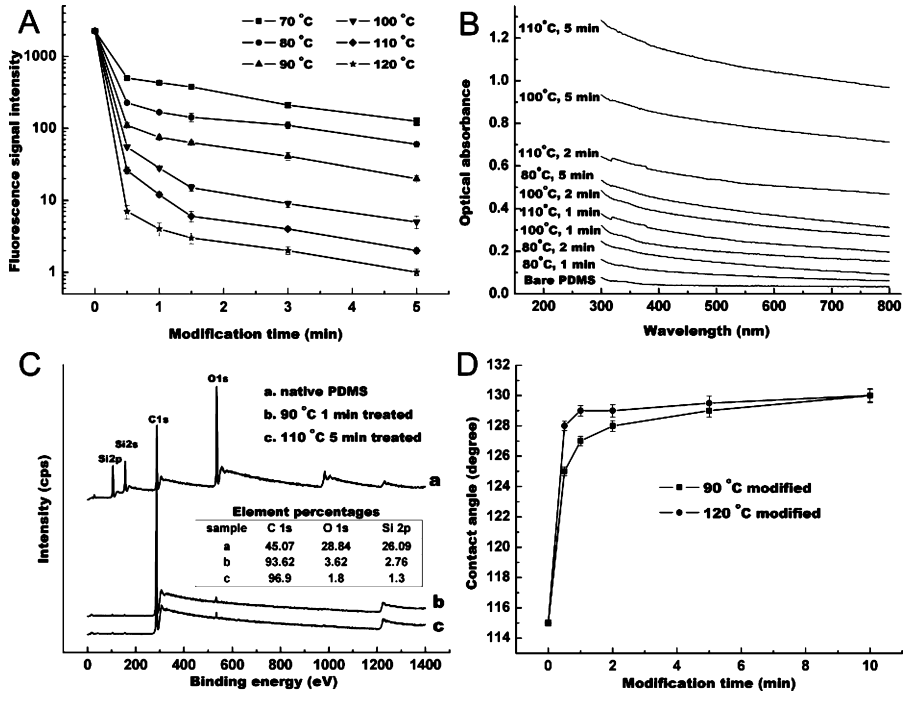

Figure 6. (A) Fluorescence intensity of rhodamine B (contacted with PDMS for 3 min and then rinsed with deionized water) absorbed by PDMS that was modified by paraffin wax at different temperatures and for different times. The fluorescence data were obtained by first averaging the signal of the sample area in the related profiles (as shown in Figure 5) and then normalizing them to the same exposure time. (B) Absorbance spectra of PDMS that was modified with paraffin wax in different conditions. The PDMS pieces were 20 mm long, 10 mm wide, and 1 mm thick. (C) XPS spectra of the surface of unmodified PDMS and PDMS modified with paraffin wax (100 °C, 1 min). (D) Advancing contact angle of water on the modified PDMS surface.

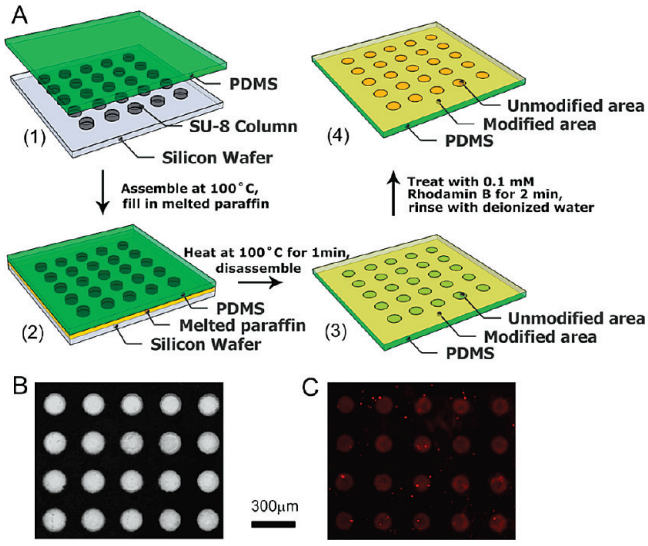

Figure 7. Patterned modification on the PDMS surface and rhodamine B absorption test. (A) Process of patterned modification of the PDMS surface and absorption test using rhodamine. (1) The PDMS slip was pressed against the SU-8 mold (the columns on the mold had a diameter of 150 μm), and they were heated to 100 °C. (2) Melted paraffin was filled into the channel between the PDMS and the mold; the modification procedure took 1 min at 100 °C. (3) The PDMS was peeled from the mold. (4) A 0.1 mM concentration of rhodamine B was dropped onto the PDMS surface and left there for 2 min; extra rhodamine B was rinsed away with DI water. (B) Wide-field microscope image of the selectively modified PDMS. Note that the image was taken under the autocontrast of the CCD program, and the real difference of transparency was not as significant as shown by the image. (C) Fluorescent image of the selectively modified PDMS after contact with rhodamine B. The camera exposure time was 400 ms. The scale bar is for (B) and (C).

that the PDMS surface was not covered homogeneously with paraffin wax. Then, native PDMS and PDMS that is modified with paraffin wax were both treated with oxygen plasma (1 min) and also characterized. The modified PDMS exhibits a greater contact angle (55°) than unmodified PDMS (20°), which might indicate that the formation of hydrophilic functional groups is more difficult on modified PDMS than unmodified PDMS.

Patterning PDMS That Is Modified with Paraffin Wax. We patterned the surface of PDMS with regions that are modified by paraffin wax (Figure 7). We fabricated a flat PDMS substrate that contained an array of disks that were unmodified by holding the substrate against an array of 150 μm diameter and 100 μm tall columns made from the SU-8 photoresist; we filled the space between the PDMS substrate and SU-8 photoresist with paraffin wax, which modified the PDMS substrate except where the columns of SU-8 photoresist were in contact with the PDMS. The results of experiments similar to those described previously confirmed that we patterned regions of PDMS that were not modified by paraffin wax and these regions selectively absorbed small molecules.

We also investigated whether PDMS that was modified with paraffin wax could be sealed to another (unmodified) PDMS surface, so that microfluidic devices could be constructed that might use the new material properties of our modified PDMS. We discovered that sealing these two surfaces after treatment with oxygen plasma was strong enough for general use (Figure S2, Supporting Information); moreover, using an oxygen plasma followed by heating in an oven (80 °C, 1 h) produced microchannels through which we flowed compressed air without disrupting the sealed surfaces.

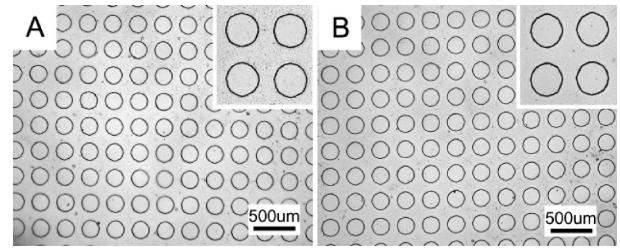

Figure 8. Images of a PDMS master (A) and a PDMS replica fabricated from it (B) taken under a microscope.

Making the PDMS Replica from the PDMS Mold. Replicating topographically patterned PDMS using polymers is a rapid method for the fabrication of complex microstructures without using photolithography; however, the process requires the surface of the "master" mold to not bind to the "replica" mold during the molding process. Researchers use typically a perfluorinated silane to prevent reactivity between the master and replica molds; however, the silanization process requires several hours to provide sufficient protection during replication.[27] We demonstrated that PDMS that is modified with paraffin wax can be used as a master to replicate several molds that show high fidelity; however, no silanization is required (Figure 8). The paraffin wax prevents cross-linking between the master and the replica molds during molding, the separation of the replica from the master is convenient;, and the replica mold exhibits the same optical, wetting, and bonding properties as typical PDMS molds. The typical number of molds that can be replicated using a template of paraffin-coated PDMS is 2−5; however, the modification could be applied repeatedly, so the number of replicas could be numerous.

Micellar Electrokinetic Chromatography (MEKC) Analysis. We compared the MEKC separations of two fluorescent dyes, sodium fluorescein and rhodamine 6G, on native PDMS and wax-modified PDMS microchips (Figure 9). The separation running condition was the same for both chips, i.e., 20 mM borax solution (pH~9.1) containing 0.25% SDS as the running buffer and a 300 V/cm field strength for separation. Figure 9A schematically shows the microchip design for the chips with "pinched" injection. Both chips could successfully separate the two dyes (Figure 9B), but there were strong differences in the separations. In native PDMS, a clear fluorescent image of the "pinch" injection area was left after the separation and the walls of the sample inlet channel were fluorescently bright; both phenomena indicated that the fluorescent molecules rapidly absorbed into (and adsorbed onto) the PDMS channel walls. In contrast, it was found that the wax-modified PDMS channels were not fouled (Figure 9C).

We also compared the fluorescent signal of rhodamine 6G with different concentrations 2 cm downstream from the injection point in the separation channels (Figure 9D). In the wax-modified channel, the fluorescence intensity of the dye increased linearly

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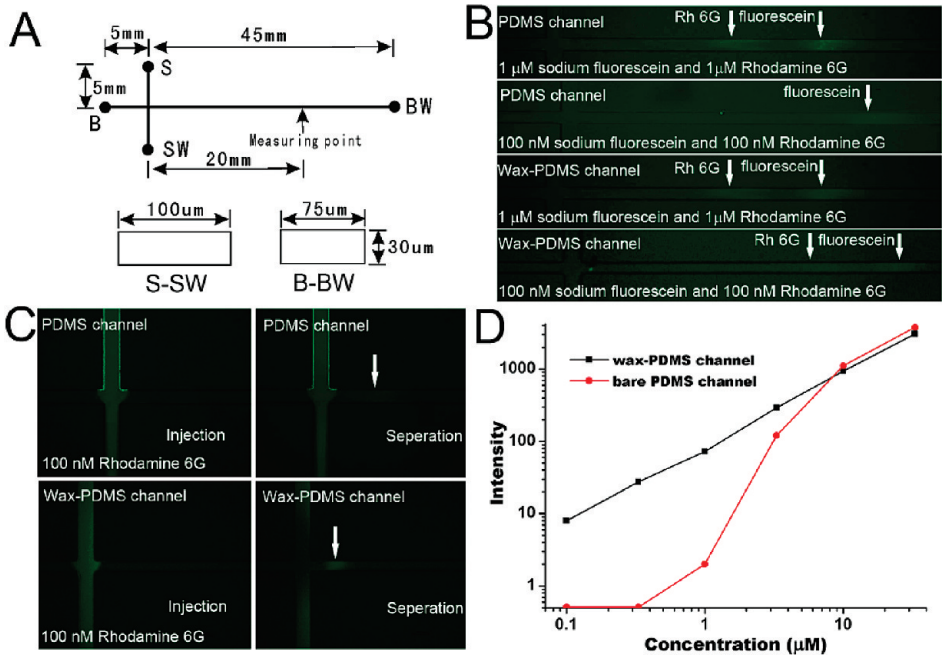

Figure 9. MEKC separations on native PDMS chips and wax-treated (100 °C for 1 min) PDMS chips. (A) Schematic chip design. (B) Fluorescent images of MEKC separations of fluorescein and rhodamine 6G. (C) Fluorescent images of pinch injection channels after separation. (D) Fluorescence intensity of rhodamine 6G in the separation channels 2 cm from the injection point on the chips.

with its concentration; even at low concentrations (100 nM), the fluorescence intensity could be clearly observed. In the bare PDMS channel, the fluorescence intensity was approximately the same as that in the wax-modified channel when the dye concentration was high; however, at low concentrations, the fluorescence intensity was much lower than that in the wax-modified channel because more dye molecules (relative to the total amount of dye molecules) are absorbed into the channel sidewalls during their migration in the separation channel. In particular, at concentrations lower than 300 nM, the rhodamine 6G band disappeared completely at the observation location.

CONCLUSIONS

In this paper we describe a simple, quick, and low-cost method for the modification of the surface of PDMS with paraffin wax. The method produces modified PDMS that resists the absorption of small molecules and that is gastight. Several factors that affect the method of modification as well as the characteristics of the modified PDMS were described. Compared with other methods, this method is more convenient, does not require solvents and hazardous chemicals, and is also rapid (<5 min) and cheap. We demonstrated that PDMS that is modified with paraffin wax can be used as a master for producing replicas, which requires only 1% of the time of existing methods. The wax-modified PDMS channels also show superior performance compared to bare PDMS in quantitative analysis. We believe that this method will be useful for quantitative microfluidics as well as for the fabrication of microchips.

ACKNOWLEDGMENT

This work was supported by a DuPont Young Professor Grant and a grant from the Hong Kong RGC (604509 and N_HKUST617109). We gratefully acknowledge postgraduate support from the HKUST NSNT program.

SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

Received for review February 10, 2010. Accepted June 10, 2010.

AC100830T