FABRICATION AND CHARACTERIZATION OF PARYLENE C-CAULKED PDMS FOR LOW-PERMEABLE MICROFLUIDICS

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ABSTRACT

This paper proposed a simple and effective fabrication method of Parylene C-caulked PDMS (pcPDMS) for low-permeability required microfluidics applications. Parylene C was deposited into PDMS to caulk the permeable sites and then the over-deposited Parylene C on top of PDMS surface was etched off by oxygen plasma. A buffered hydro-fluoride acid treatment was adopted to recover the over-oxygen-plasma-treated PDMS surface for the following pcPDMS-pcPDMS bonding. Scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) were used to characterize the Parylene C caulked status in the PDMS matrix. Dynamic diffusions of Rhodamine B inside the native PDMS and the pcPDMS were experimentally compared. The preliminary results indicated that the proposed pcPDMS can dramatically suppress the diffusion of small molecules into the PDMS matrix, making it suitable for corresponding microfluidics applications.

INTRODUCTION

Poly(dimethylsiloxane) (PDMS) is an excellent material for a wide variety of microfluidics applications, as it is easy to fabricate, optically transparent, biocompatible, and cheap enough for massive usage. However, as questioned by Mukhopadhyay R. [1], there are several issues with PDMS when it is applied in biomedical research, among which diffusion of small molecules into the PDMS matrix due to its porous nature is the most serious one and still problems [2]. For instance, the porosity of PDMS generated bubbles inside microchamber(channel) and caused sample evaporation in a PDMS PCR chip, which made the DNA amplification inside failed [3]. In the *in situ* microfluidic temperature visualization technique with the Rhodamine B as the temperature indicator, the dye diffused into the PDMS matrix, and resulted in a fake temperature variation [4]. The porous essence of PDMS also affects its surface zeta potential and consequentially degrades the electroosmotic performance to some extent [5].

Many research groups have attempted to solve this problem by modifying the surface properties of PDMS. A commonly used method is to chemically graft PDMS surface with some polymers, such as polybrene [4], poly(urethaneacrylate) [6], and other epoxy-modified polymers [7], as a static surface coating. These chemical modifications are usually time-consuming, complex and their chemical reliabilities are still questionable. Another method is dynamically coating the inner surface of PDMS microchannel, for instance, sodium dodecyl sulphate was added to the fluid to suppress diffusion of Rhodamine B into PDMS matrix [8]. However, the additive changes the working fluid and limits its applications. Similarly, Abate et al. proposed a method to coat the inner surface of PDMS channels with a glass-like layer using sol-gel chemistry [9], and the diffusion of Rhodamine B into the bulk PDMS substrate was prevented. The glass-like coating not only changes the cross-sectional shape and dimension of microchannels, but also makes the PDMS device fragile and uneasy to deform. In a different way, Roman et al. fabricated PDMS microchips with SiO_2 particles homogenously distributed within the PDMS matrix, and the modified PDMS showed no Rhodamine B diffusion during a 4h test [10]. They also expanded this method to transition metals, i.e., the metal alkoxides diffused into the substrate of a PDMS channel resulting in a metal oxide modified PDMS surface [11]. Recently, Ren KN et al. introduced a method to modify PDMS with paraffin wax [12]. Paraffin can diffuse into the bulk PDMS and generates a hybrid material that restricts diffusion of small molecules into PDMS. In the above hybrid material generation strategies, the protocols all relied on heavy manual operations and were incompatible with traditional microfabrication process, which make their effectiveness and productivity arguable.

Sawano et al. demonstrated a method for low-permeability required pneumatic application by depositing Parylene C into PDMS [13]. Parylene C monomers effectively permeated the bulk PDMS and sealed the permeable sites and so-named Parylene C-caulked PDMS (pcPDMS) was achieved. The surface Parylene C layer on top of the PDMS was removed by oxygen plasma etching to restore the elastic features of PDMS. Therefore this pcPDMS can provide low permeability and high elasticity for flexible actuator applications. However, this pcPDMS is not ready for microfluidic applications because it is difficult to be bonded with other substrates as its original status [14]. The over-oxygen-plasma-treated PDMS, generated during the removal of surface Parylene C, is still a barrier for further oxygen plasma induced pcPDMS-pcPDMS bonding.[15]

This paper proposes a simple and effective fabrication method for pcPDMS for low-permeability required microfluidics applications. Buffered hydro-fluoride acid (BHF) was used to clean the barrier layer on top of the pcPDMS after a long period oxygen plasma treatment. Scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) were used to characterize the Parylene C caulked status in PDMS matrix. Dynamic diffusion performances of Rhodamine B in the native PDMS and the pcPDMS were compared experimentally.

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METHOD AND EXPERIMENTS

Fabrication process of a typical pcPDMS microfluidic device was schematically illustrated in Figure 1. Flat PDMS and PDMS microstructures were prepared by casting and replica molding (a). Then Parylene C layer was deposited onto the PDMS substrates. During the Parylene C deposition, the monomers permeated into the PDMS matrix and sealed the permeable sites. Over deposited Parylene C formed a thin film on top of the PDMS surface (b). Then oxygen plasma was used to etch the unnecessary Parylene C off (c). After removal of this Parylene C thin film, a silica-like layer was generated on the surface because the long term oxygen plasma treatment ashed the methyl groups of PDMS molecules and left its silicon-backbone exposed [16]. This silica-like layer was believed the main origin of the aforementioned bonding barrier. Herein, buffered hydro-fluoride acid (BHF) was used to treat the PDMS surface (d). Finally, the BHF treated pcPDMSs were successfully bonded by a traditional oxygen plasma bonding technique (e).

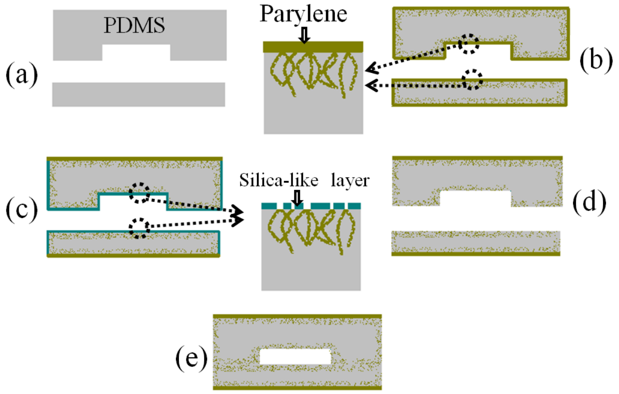

Figure 1: Fabrication process of the pcPDMS microchannel, (a) preparation of flat PDMS and PDMS microstructures, (b) Parylene C deposition, (c) removal of surface Parylene C by oxygen plasma etching, (d) removal of the silica-like layer by BHF etching and (e) pcPDMS bonding by oxygen plasma treatment.

PDMS preparation

Silicon masters were prepared by traditional photolithography and ion coupled plasma silicon etching (ICP) for microchannels. PDMS (SYLGARD 184, Dow Corning Toray Co., Ltd) was mixed at a 10:1 base to curing agent mass ratio. The PDMS prepolymer was degassed in a vaccum desiccator, poured onto the masters and then cured at 60^{o}C for 1h. The cured PDMS were peeled off from the masters, and holes were punched as reservoirs. The microchannel had a dimension of 10 mm long, 170 µm wide and 20 µm deep. Flat PDMS were prepared by casting the prepolymer mixture onto a flat wafer with a same curing condition as the aforementioned.

Parylene C deposition

PDMS samples were coated with Parylene C in a chemical vapor deposition system (PDS 2010, SCS, USA). The working pressure of the deposition chamber was set as 2.13 Pa for a low deposition rate to facilitate the penetration of Parylene C monomers into the bulk PDMS. The thickness of the Parylene C was controlled by the amount of the loaded dimmer. In this work, 1.0 g dimmer was consumed to form a Parylene C film of about 800 nm thick (measured on a bare silicon wafer which was deposited along with the PDMS samples).

pcPDMS-pcPDMS bonding

Oxygen plasma etching was used to remove the surface Parylene C on top of the PDMS substrate. Parameters of the oxygen plasma etching are optimized as: oxygen flow rate 1500 sccm, chamber pressure 35 Pa, and etching power 100 W. Parylene C-coated PDMS and native PDMS samples were both exposed in the oxygen plasma for 240s. Then, so-obtained pcPDMS and over-oxygen-plasma-treated PDMS were dipped in BHF (HF:NH_4F=1:4, v%) solution for 10 s to get rid of the silica-like layer. After rinsed in DI water and dried in nitrogen gas, patterned and flat pcPDMS were tried bonding by oxygen plasma treatment with an activating time of 5 s. Native PDMS and over-oxygen-plasma-treated PDMS plus BHF treating were also bonded for comparison.

SEM characterization

Surface topography of native PDMS, PDMS after BHF treatment, and pcPDMS was examined under scanning electron microscopy (SEM). All samples were sputter-coated with W (< 5 nm) for SEM observation.

XPS characterization

XPS spectra were taken on an Imaging Photoelectron Spectrometer (Axis Ultra, Kratos Analytical Ltd.). Elemental composition was calculated on peak areas from the C 1s, O 1s, Si 2p, Si 2s, and Cl 2p core levels. Element Cl is the indicator of Parylene C as illustrated in Figure 1. Native PDMS, Parylene C coated PDMS and Parylene C-caulked PDMS were examined. For pcPDMS sample, the surface layer was tested first, and then the measurement was carried out after the surface was etched by argon plasma to investigate the bulk status. Sequentially etching at 150s, 350s, 750s, 1350s, 2150s were used to get a depth profile of Cl distributions inside the bulk pcPDMS. The overall depth was estimated to be 215 nm based on an empiric etching rate of 6 nm/min.

Rhodamine B diffusion measurements

Rhodamine B (Sigma, S9012) at a concentration of 150 µM in DI water was injected into the microchannels constructed by native PDMS, PDMS with over-oxygen-plasma-treatment plus BHF clean, and pcPDMS. The large reservoirs guaranteed that the channels were filled with constant-concentration Rhodamine B during the testing period. Fluorescent intensities inside the channels were imaged at 0 min, 5 min, 20 min, and 60 min after sample loading by a microscope (BSF-50, Shanghai Batuo Instrument Co. Ltd) with a CCD camera. During the measurement, the chips were kept in the dark to prevent photobleaching. Fluorescent intensities of each image were analyzed by MATLAB.

RESULTS AND DISCUSSIONS

Surface topography

SEM images were taken to examine the surface topography of native PDMS, PDMS treated by BHF, and pcPDMS, as shown in Figure 2. The native PDMS (a) surface is flat and smooth, and BHF treating has no significant effect on PDMS (b). The web-shaped nanoscale patterns, which were homogeneously distributed on the pcPDMS sample (c), are the evidences of the Parylene C that were uniformly caulked into PDMS matrix.

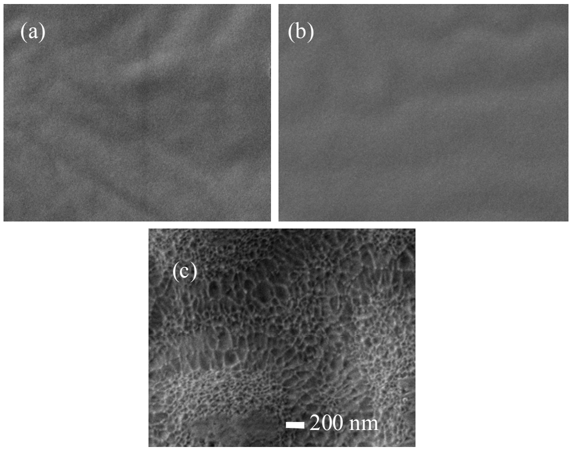

Figure 2: SEM photos of the surface morphologies of the native PDMS surface (a), the PDMS surface after BHF etching (b) and the pcPDMS surface (c).

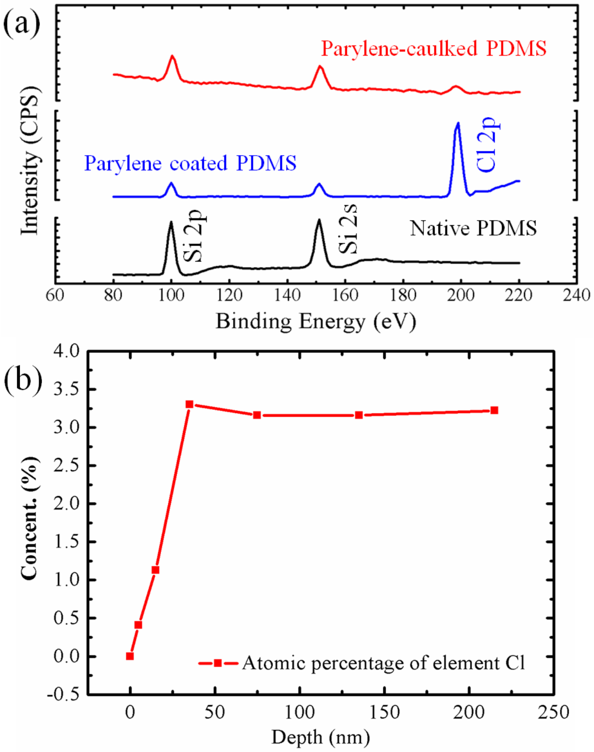

Figure 3: (a) XPS Cl 2p, Si 2p and Si 2s spectra of native PDMS, Parylene- coated PDMS and pcPDMS. (b) Atomic percentage of Cl along the depth of pcPDMS from the surface.

XPS characterization

The presence of Parylene caulked in PDMS was further proved by X-ray photoelectron spectroscopy (XPS) characterizing. Figure 3(a) shows the obtained XPS spectra of native PDMS, parylene C-coated PDMS and Parylene-caulked PDMS at peaks of Si 2p, Si 2s and Cl 2p, respectively. Parylene-coated PDMS gave peaks at 200.4 eV due to chlorine (2p) that is the indicator of Parylene C, and the same peak was observed in the spectrum of pcPDMS sample, but was not found in that of native PDMS. Figure 3(b) presented the chlorine percentage variation deep into the bulk matrix of pcPDMS sample. It can be concluded that Parylene C successfully penetrated into the bulk PDMS with a depth more than 200 nm.

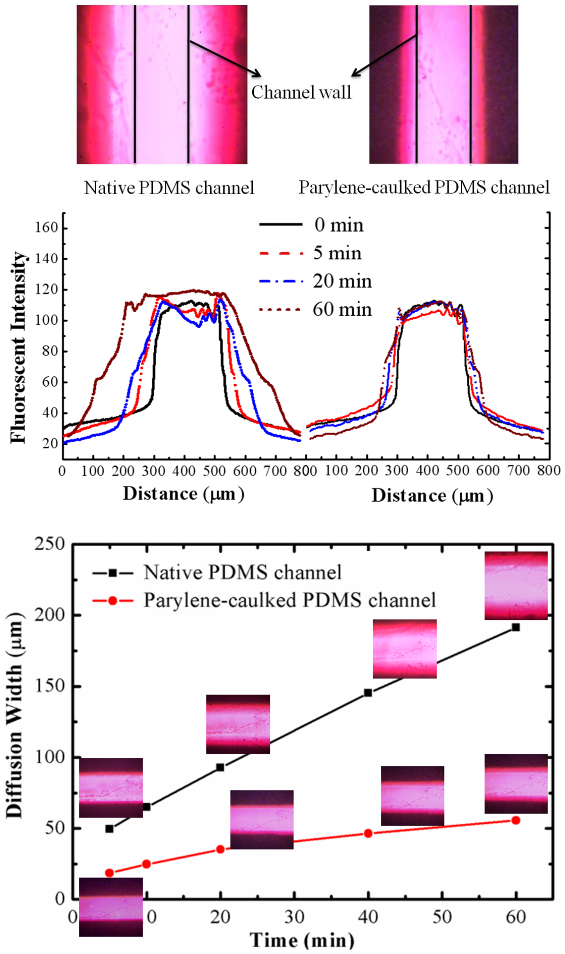

Figure 4: (a) Fluorescent intensities of Rhodamine B in the native PDMS and the Parylene-caulked PDMS channels (170μm wide) at 0 min, 5 min, 20 min and 60 min after the sample loading. The photos above were taken 60 min after the sample loading. (b) Relationship of Rhodamine B diffusion width with time in the native PDMS and the Parylene-caulked PDMS channels (170μm wide).

Dynamic diffusion of Rhodamine B

Fluorescent intensities of Rhodamine B in native PDMS and pcPDMS microchannels at 0min, 5min, 20 min, and 60 min right after the sample loading were shown in Figure 4(a).

Clearly, there were large amounts of Rhodamine B diffused into the native PDMS, while the diffusion was significantly suppressed in the pcPDMS microchannel. The dynamic diffusion length of Rhodamine B into native PDMS and pcPDMS within 60 min were calculated, as shown in Figure 4 (b). The nominal diffusivity of Rhodamine B in the native PDMS was calculated as $3.5\times10^{-9}m^2/s$, which was almost 19 times larger than that in the pcPDMS, $1.8\times10^{-10}m^2/s$. Diffusion of Rhodamine B cannot be completely prevented in the present pcPDMS because Parylene C did not coat the entire inner surface, and the permeable mechanism for this hybrid material needs further investigations. Dynamic diffusion of Rhodamine B in the PDMS channel with over-oxygen-plasma-treatment plus BHF clean was also studied and the results (not shown here) showed insignificant difference with the native PDMS sample.

CONCLUSIONS

This work presented an simple and effectivce mehtod to prepare low permeability hybrid material, Parylene C-caulked PDMS, and the corresponding fabrication protocol for its applications in microfluidics. The difficulity in bonding of PDMS/pcPDMS that undergone long time oxygen plasma treatment was succesfully overcomed by introducing a BHF treatment to recover the PDMS surface. The presence of Parylene C caulked inside PDMS was proved by SEM and XPS characterizations. The PDMS microchannels with Parylene C-caulked showed low permeability to small molecules as the diffusion of Rhodamine B was significantly suppressed. Parylene C layers on the surface of this pcPDMS chips could be retained in the present method, which can also serve as sealing layers to decrease its permeability to gases. Surfce chemisty of this pcPDMS is not essentially changed, as Parylene C is also biocompatible, the present pcPDMS is suitable for versitile biomedicine relevent applications.

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