

Glass coating for PDMS microfluidic channels by sol–gel methods†

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Soft lithography using polydimethylsiloxane (PDMS) allows one to fabricate complex microfluidic devices easily and at low cost. However, PDMS swells in the presence of many organic solvents significantly degrading the performance of the device. We present a method to coat PDMS channels with a glass-like layer using sol–gel chemistry. This coating greatly increases chemical resistance of the channels; moreover, it can be functionalized with a wide range of chemicals to precisely control interfacial properties. This method combines the ease of fabrication afforded by soft-lithography with the precision control and chemical robustness afforded by glass.

Polydimethylsiloxane (PDMS) is widely used for fabrication of microfluidic devices: it is inexpensive and it can be fashioned to have complex channel structures.^{1,2} Sophisticated channel designs can be “stamped” with high fidelity into a PDMS slab with a mold that can be reused many times. This holds great potential for scale-up and the high-volume production of inexpensive devices capable of performing sophisticated functions. Despite these advantages, PDMS channels have several drawbacks. Even when cured, PDMS remains permeable to liquids and gases.^{1–4}

Such permeability can affect reactions that occur in the channels. Organic solvents can swell PDMS significantly⁴, seriously degrading device performance. The limited chemical compatibility of PDMS is, therefore, a major problem that can limit the wider application of PDMS to microfluidic technology.⁴ This has motivated development of other materials that combine simplicity of fabrication with chemical robustness.^{5–7} Alternatively, attempts have been made to decrease the permeability of PDMS by modifying the surface. For example, by infusing PDMS channels with transition metal oxide precursors, the diffusion of small molecular weight dye molecules can be suppressed.^{8,9}

Similarly, by coating PDMS slabs with poly(urethaneacrylate), swelling due to organic solvents can be retarded.¹⁰ Indeed the most chemically inert and controllable material for making microfluidic devices is glass; however, glass is much more difficult to pattern and manipulate to form the requisite devices. Thus, an optimal system would combine the ease of fabrication and simplicity of PDMS with the chemical robustness and precise control of the interfacial properties of glass.

In this communication we present a simple method that combines the ease of fabrication of PDMS with the robustness of glass. We use sol–gel chemistry to coat the channels of PDMS microfluidic devices with a chemically resistant glass layer whose surface properties can be controlled. Such coatings are widely used to provide protection against aggressive solvents and to greatly increase corrosion resistance of industrial parts.¹¹ Unlike glass, they can be deposited and cured at room temperature. To test the chemical resistance of the coated channels, we use aqueous Rhodamine B, an organic dye that diffuses into PDMS, and toluene, an organic solvent that dramatically swells PDMS. We show that the coating prevents Rhodamine B from diffusing into the PDMS and suppresses swelling of the channels when exposed to toluene. We also illustrate the ability to functionalize the surface of the coated channels by fabricating flow-focusing drop makers that produce both water-in-toluene and toluene-in-water emulsions.

For the sol–gel chemistry, we use tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES) as precursors. However, these chemical precursors can swell and dissolve PDMS. To prevent swelling, we oligomerize, or

preconvert, the precursors. To accomplish this, we add acid, which catalyzes condensation and hydrolysis reactions of the alkoxy silanes.¹²

The original silane monomers grow into higher molecular weight silane oligomers through reactions with one another. Hydrolysis reactions also cleave ethoxy groups from the silanes converting them into hydroxyl groups. The resulting larger oligomer precursors are less miscible with PDMS, preventing swelling. In addition, preconversion also reduces contraction and cracking during gelation, yielding more homogenous coatings.

To prepare the preconverted sol mixture we combine TEOS, MTES, ethanol, and pH 4.5 water adjusted with HCl in a 1 : 1 : 1 : 1 volumetric ratio. We speed the mixing process by heating the mixture in a microwave oven for 10–20 s. The homogenous mixture is then placed in a 65 °C oven for 12 h to speed preconversion. The PDMS channels are treated with oxygen plasma to generate hydroxyl groups just before they are bonded to the bottom plate, which can either be a glass slide or another slab of PDMS. The bonded device is then immediately flushed with the preconverted sol mixture.³

The preconverted siloxanes react with the hydroxyl groups to form covalent bonds with the PDMS. To initiate the gelation reaction the device is placed on a 100 °C hotplate. After 10 s, 10 mL of air is used to flush out the sol. This takes about two minutes and leaves behind the desired coating. The thickness of the coating increases with the time on the hotplate before the precursor mixture is flushed with the air. This enables the coating thickness to be controlled and allows the glass coating to be tailored to achieve the desired dimensions of the channels. The chemical composition of the precursor mixture, preconversion time and temperature, and curing temperature can also all be varied to control sol–gel properties, enabling further control of the coating properties.^{12–16}

To directly observe the sol–gel coating we use scanning electron microscopy (SEM) and image both uncoated and coated channels. The uncoated channels are initially rectangular in shape and exhibit clean PDMS walls, as shown in [Fig. 1a](#). By contrast, when coated, the cross-section of the channels are rounded due to the thick coating deposited on the walls, as shown in [Fig. 1b](#). From the images we estimate the coating thickness to be about 5–10 µm.

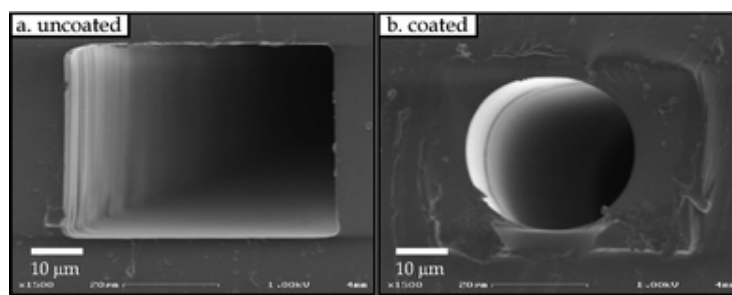


Fig. 1 Scanning electron micrographs of cross-sections of (a) uncoated and (b) coated PDMS channels. The original channel dimensions are 50 × 35 µm.

To determine the degree of chemical resistance of the coating we perform two experiments. The first experiment tests the diffusion of a solute from an aqueous phase into the PDMS. We use Rhodamine B, a fluorescent organic molecule that diffuses into cured PDMS, and can therefore be used as a fluorescent probe of chemical resistance.^{8,9}

We prepare coated and uncoated channels and fill them with a 50 µM aqueous solution of Rhodamine B. The channels are then stored in the dark for four days and the water is allowed to evaporate. Rhodamine B diffuses into the walls of the uncoated channels, as shown in [Fig. 2a](#). By contrast, there is no diffusion whatsoever into the walls of the coated channel; instead, the fluorescence is all contained on the surface of the channel, as shown in [Fig. 2b](#)

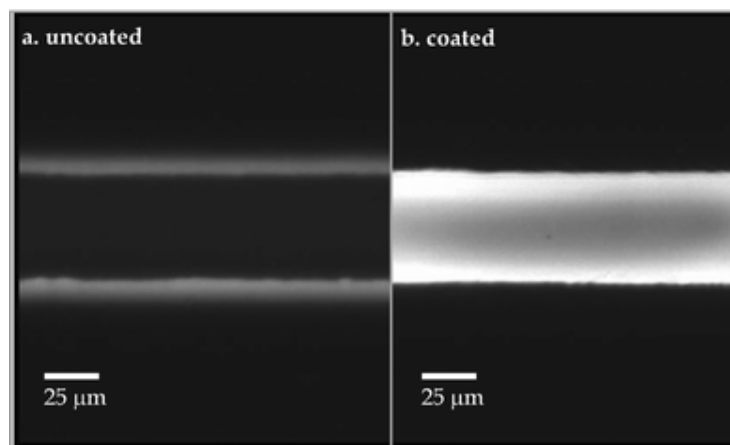


Fig. 2 Comparison of diffusion of Rhodamine B for PDMS channels. (a) Uncoated PDMS channel in which Rhodamine B has diffused into the walls. (b) Coated PDMS channel in which diffusion of Rhodamine B has been prevented, leaving a light layer of dye on the surface of the coating.

The second experiment tests the swelling of the PDMS channels due to an organic solvent. We use toluene, an organic solvent commonly used in chemical synthesis, which significantly swells PDMS.^{4,10} We flow toluene through coated and uncoated PDMS channels at 100 $\mu\text{l/hr}$ using syringe pumps and measure the time evolution of the shape of the channels. The size of the initial, empty channels at $t = 0$, is shown in the optical images in [Fig. 3a](#) and [Fig. 3b](#). Due to the cylindrical shape of the coated channel and the index of refraction mismatch of the coated channel with air, an optical lensing effect can be seen in [Fig. 3b](#). By contrast, the uncoated channel does not show this effect. At $t = 0.57$ s, both channels have been filled with toluene; already the uncoated channel has begun to swell and has become narrower, as shown in [Fig. 3c](#). By contrast, the coated channel remains unswollen; because of the smaller mismatch of the index of refraction, the lensing effect has vanished to reveal a smooth sol–gel coating, shown in [Fig. 3d](#). At $t = 13$ s the uncoated channel has further swollen and the walls have nearly reached their final swollen state, [Fig. 3e](#). By contrast, the coated channel remains unchanged, [Fig. 3f](#). Even after an hour of use, the coated channel has changed very little. These experiments demonstrate the robustness of the glass coating as a chemical barrier for the channels.

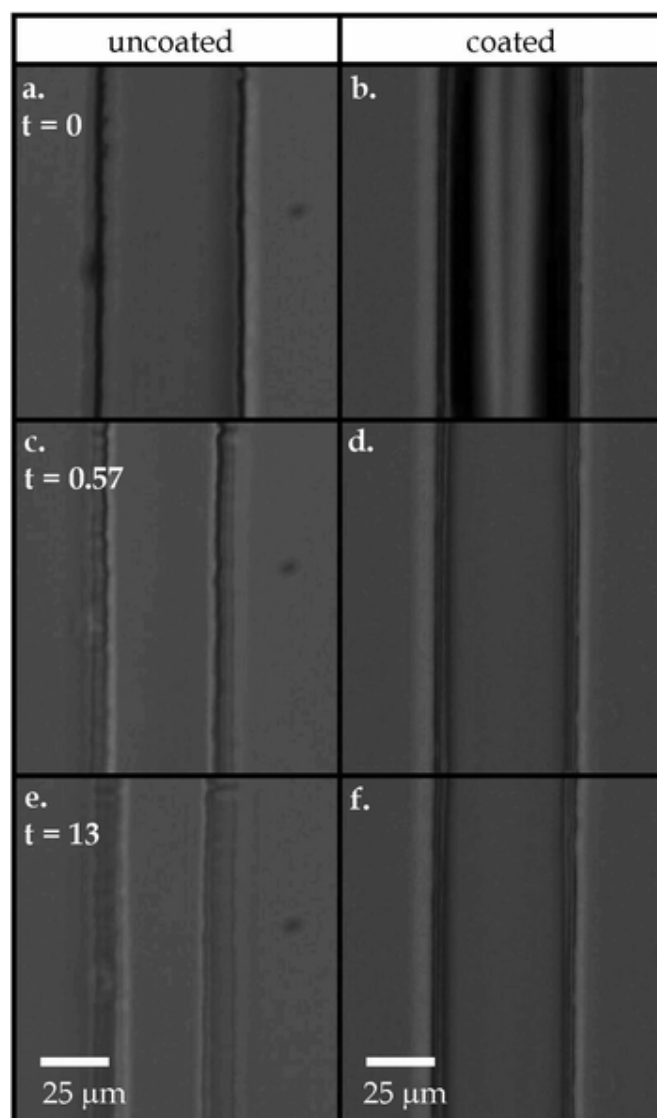


Fig. 3 Comparison of swelling of PDMS due to exposure to toluene. Each row contains an image of the uncoated and coated channels at a time, t , after the flow is initiated. Uncoated (a) and coated (b) channels at $t = 0$ s just prior to exposure to toluene so that the channels are empty. Uncoated (c) and coated (d) channels at $t = 0.57$ s. Toluene has just started flowing through the channels and, already, the uncoated channel has begun to swell. Uncoated (e) and coated (f) channels at $t = 13$ s. The uncoated channel has further swollen and the walls have nearly reached their final swollen state. By contrast, the coated channel remains unchanged.

In addition to providing a chemical barrier against organic compounds, the glass coating can be functionalized to have a variety of chemical properties. This is particularly important for production of emulsions where the surface must have preferential wetting characteristics to ensure that drops are formed.¹⁷ To illustrate this, we produce emulsions using water and toluene. We use a flow focusing drop making device¹⁸ coated using our sol-gel procedure. We use only a single inlet to fill and flush the coating mixture; more inlets could be used to coat more complex channel structures. We also reduce the initial time on the hotplate to 5 s thereby depositing a thinner coating, since the channel dimensions are smaller. After coating the channels, we functionalize the device to control the wetting properties. We make one device hydrophobic by treating it with AquapelTM. This is

accomplished by filling with Aquapel™

and then immediately flushing with air, leaving a thin coating on the surface. This device produces inverted emulsions consisting of water drops in toluene as shown in [Fig. 4a](#). We make an identical device hydrophilic by treating it with preconverted N-[3-(Trimethoxysilyl)propyl] ethylene diamine. The device is filled and allowed to sit for 5 min, and then flushed out with air. This device produces direct emulsions consisting of toluene drops in water as shown in [Fig. 4b](#).

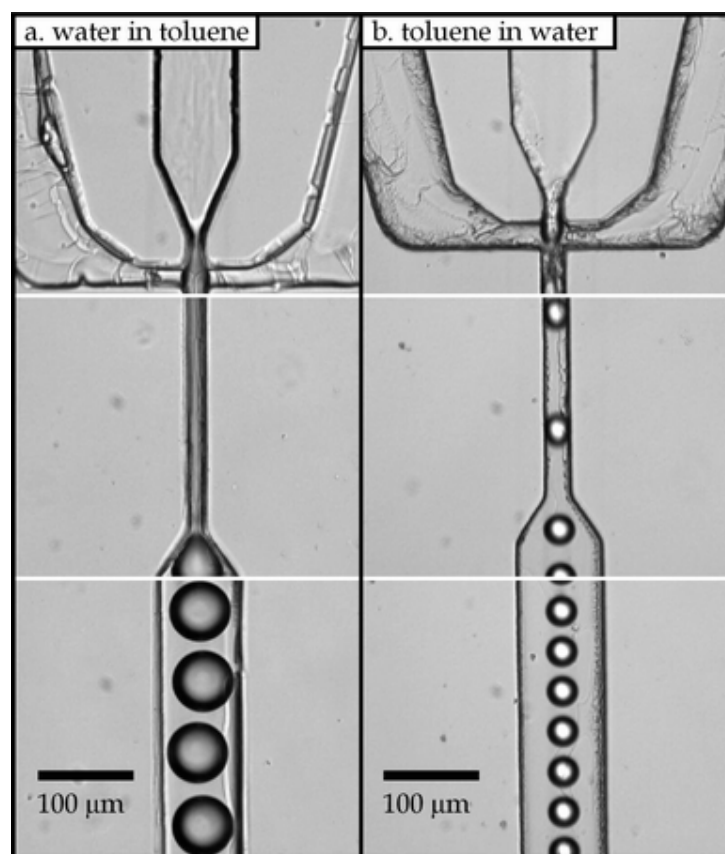


Fig. 4 Direct and inverted emulsions generated in coated and functionalized flow-focusing devices. (a) Inverted emulsions consisting of water-in-toluene drops produced at flow rates $500/500 \mu\text{l h}^{-1}$ inner/outer phase. The coated channels were made hydrophobic by application of Aquapel. (b) Direct emulsion consisting of toluene-in-water, produced at flow rates $150/500 \mu\text{l h}^{-1}$ inner/outer phase. The channels were made hydrophilic by application of preconverted N-[3-(trimethoxysilyl)propyl] ethylene diamine, ethanol, and pH 2 water adjusted with HCl in a 1 : 1 : 1 volumetric ratio.

The glass coating changes the shape of microchannels. The particular shape and dimensions of the coated channels can be adjusted by controlling the original channel dimensions and the thickness of the applied coating. This allows the channel dimensions to be engineered and adjusted to the desired size. Moreover, it provides a method to produce channels with cylindrical symmetry rather than square symmetry, since the glass wets the surface and collects in the corners. The glass coating significantly improves the performance of PDMS microfluidic devices. It provides a protective barrier that greatly increases the chemical resistance of the PDMS microchannels. In addition, the coating can be functionalized to have a wide range of surface properties. This can be exploited, for example, to produce both direct oil-in-water and inverted water-in-oil emulsions in coated channels using organic solvents. The collection of these attributes significantly broadens the applicability of

PDMS to microfluidic technology, enabling its use in a much wider class of systems and for a greater variety of chemicals. It combines the scalability and simplicity of stamped PDMS devices with the chemical versatility and robustness of glass.

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Footnotes

† Electronic supplementary information (ESI) available: Experimental details and the movies of emulsion generation using flow-focusing devices. See DOI: [10.1039/b800001h](https://doi.org/10.1039/b800001h)

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