IN-SITU SOL-GEL MODIFICATION OF PDMS ELECTROPHORETIC ANALYTICAL DEVICES

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ABSTRACT

This paper reports on a rapid new method for *in-situ* sol-gel deposition of silica layers in PDMS microchannels. A two-step process is used; first allowing TEOS to diffuse briefly into the channel, followed by acid catalysed hydrolysis and condensation. The silica coating results in an increased and stabilised electroosmotic flow. With this novel method there is no need for pretreatment of the microchannels or time consuming oligomerisation of the precursor solution. The silica coating combines the benefits of glass, such as hydrophilicity and a stable high electroosmotic flow, with the advantages of rapid microdevice prototyping offered by PDMS.

KEYWORDS: sol-gel, surface modification, tetraethyl orthosilicate (TEOS), polydimethylsiloxane (PDMS), electroosmotic flow (EOF)

INTRODUCTION

In the last decade PDMS has found extensive use in the fabrication of microchips. Its popularity is due to its low cost, optical transparency, and ease of use. However untreated PDMS surfaces lack ionisable groups and therefore only support a low electroosmotic flow. Furthermore the PDMS surfaces are hydrophobic, making them difficult to wet and hydrophobic analytes can easily adsorb onto the PDMS surface. These drawbacks make modification of the PDMS surface necessary for applications in electrophoretic separations.

Creating a robust and stable glass-like PDMS surface, by sol-gel deposition of SiO_2, is a promising surface treatment method for PDMS microchannels. Earlier work focussed on the sol-gel formation of hybrid silica/PDMS materials: Roman *et al.* [1] diffused a silica precursor solution from the outside into a constructed microchip to form silica nanoparticles throughout the bulk PDMS upon exposure to a ethylamine solution. This treatment resulted in a high electroosmotic flow, which remained stable for up to 60 days in dry storage. However, the method is time consuming, taking more than 16 hrs in total.

In our work the sol-gel layers are put directly onto the walls of the channels in a fast two-step process. Firstly, the silica precursor (TEOS) is diffused into the microchannel, followed by acid catalysed hydrolysis and condensation to form the silica layer. TEOS can swell and even dissolve the elastomer, so care must be taken not to distort and block the microchannel. To overcome this problem Abate *et al.* [2] first oligomerised the silica precursor mixture before deposition. Additionally, the PDMS microchannels were activated using oxygen plasma to covalently bond the thick glass-like coat layer. Our new method actually uses the miscibility of PDMS in TEOS: *i.e.* some penetration of TEOS into the PDMS microchannel wall produces a strong bond between the PDMS and silica layer. By using a diluted TEOS solution and only a brief diffusion time, there is no distortion of the channel geometry and the PDMS does not dissolve in the precursor solution.

EXPERIMENTAL

PDMS ((Sylgard 184 Silicone Elastomer Kit, Dow Corning) microchannels were fabricated using a SU-8 on PMMA master as described earlier by Bubendorfer *et al.* [3]. Reversibly bonded microfluidic channels, 100 µm x 20 µm x 3 cm long, are formed by contacting the PDMS channel piece with a flat PDMS piece and heating at 65°C for 1 hr. The sol-gel surface modification was performed in two steps. In the first step a TEOS (98+%, Lancaster):ethanol solution (volume ratio 1:2) was continuously flowed through the channel for 15 minutes. Secondly, after removal of the TEOS solution the channel was filled with a solution of acetic acid (100%, BDH) in deionised water (18.3 $M\Omega cm^{-1}$, Barnstead NANOPure system) at a ratio of 1:2.

Several techniques were used to analyse the sol-gel modified PDMS microchannels. Optical micrographs of the channel were obtained using a Nikon microscope with a Cascade 1K CCD camera from Photometrics. ATR-FTIR spectra were measured on a Perkin Elmer Spectrum One equipped with a Universal ATR sampling accessory with a diamond/ZnSe crystal. Static contact angle measurements were performed using a CAM200 apparatus (KSV Instruments). Electroosmotic flow measurements were carried out using the current monitoring method [4] with 20 and 18 mM KPO_4 buffer (at pH 7) and an electric field of 167 V/cm.

RESULTS AND DISCUSSION

The successful deposition of a sol-gel silica layer by the fast *in-situ* method is evident from optical micrographs of pristine (Figure 1A) and silica coated (Figure 1B) PDMS microchannels. The modified surface shows features on the channel surfaces of up to 5 µm. The average thickness of the deposited layer is estimated to be of the order of 2 µm. Analysis of the images along the complete channel showed a uniform distribution of the coating and no deformation of the channel geometry.

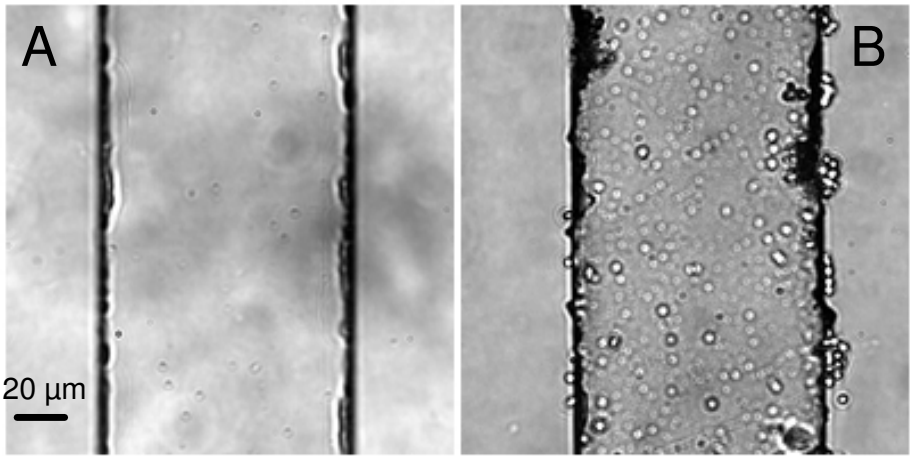

Figure 1: Optical micrographs of pristine (A) and silica coated (B) PDMS microchannels.

Besides changes in morphology, there are also changes in surface chemistry. Figure 2 shows ATR-FTIR spectra of pristine and silica coated PDMS slabs. There is a decrease in the absorbance peaks related to the -CH_3 groups associated with the PDMS polymer backbone. At the same time the absorbance associated with Si-OH and Si-O-Si groups increase after deposition of the silica layer. Furthermore, coating of the PDMS with silica led to a small decrease in contact angle from 114 to 95°, which is enough to facilitate the introduction of aqueous solutions into the channels. The increase in hydrophilicity is thought to be a direct result of the silanol groups formed on the surface.

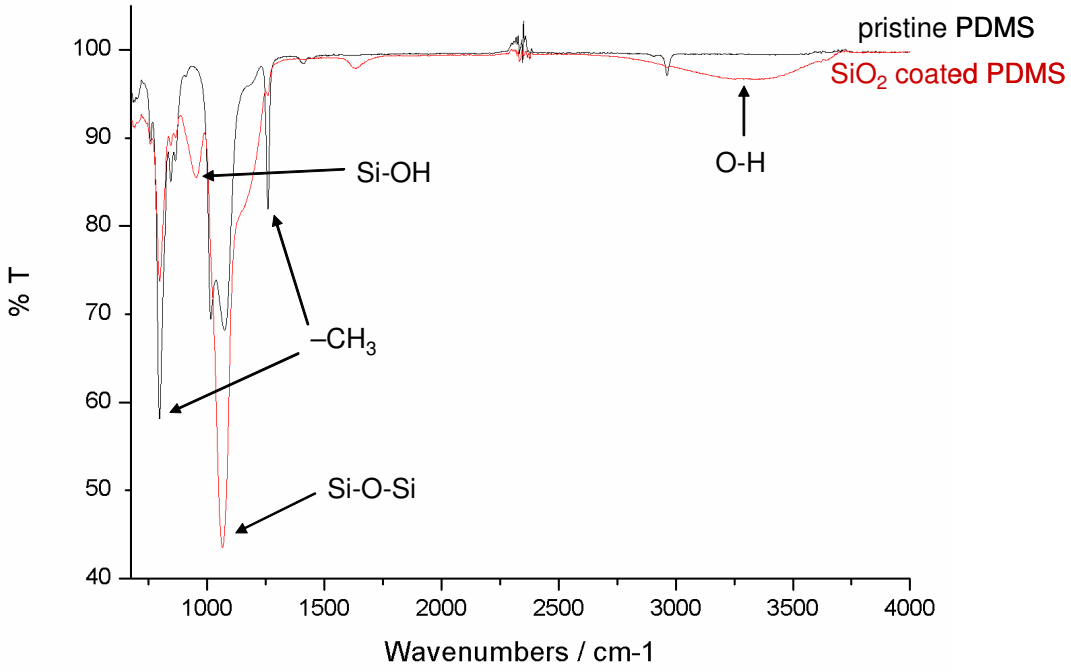

Figure 2: ATR-FTIR spectra for pristine (black line) and sol-gel silica coated PDMS (red line)

The electrokinetic characteristics are important for use of the modified PDMS in electrophoretic analytical applications. Preliminary electroosmotic flow measurements, Table 1, show a high and stable flow for the silica sol-gel modified PDMS channels in comparison with pristine PDMS channels. Over a period of a week the electroosmotic flow dropped only 10%, while pristine PDMS microchannels showed a drop of more than 30%.

Table 1. Comparison of electroosmotic flow (EOF) of silica coated and pristine PDMS microchannels.

	EOF on day 1 [cm/s]	**EOF on day 8 [cm/s]**
SiO_2 coated PDMS	0.043 ± 0.002	0.038 ± 0.001
Pristine PDMS	0.034 ± 0.001	0.023 ± 0.002

CONCLUSION

The rapid and direct method we developed selectively deposits silica on the surface of a PDMS channel by *in-situ* acid-catalysed hydrolysis. With this method there is no need for pretreatment of the microchannels or time consuming oligomerisation of the precursor solution. The silica coating in PDMS microchannels combines the benefits of glass, such as hydrophilicity, and a stable high electroosmotic flow, with the advantages of rapid microdevice prototyping offered by PDMS. Moreover, the silica surface enables functionalisation, offering the possibility for enzyme immobilisation for fabrication of bioanalytical devices.

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