A NEW METHOD OF UV-PATTERNABLE HYDROPHOBIZATION OF MICRO- AND NANOFLUIDIC NETWORKS

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ABSTRACT

This work reports a new method to hydrophobize glass-based micro- and nanofluidic networks. Conventional methods of hydrophobizing glass surfaces often create particulate debris causing clogging, especially in shallow nanochannels, or require skillful handling. Our novel method employs an oxygen plasma, silicone oil and ultraviolet (UV) light. The contact angle of the modified bare glass surface can reach 100° whilst the inner channels after treatment facilitate stable and durable water-in-oil droplet generation. This modified surface was found to be stable for more than three weeks. The use of UV in principle enables in-channel hydrophobic patterning.

KEYWORDS: Microfluidics, Nanofluidics, Surface Modification, Hydrophobization, UV light, Oxygen Plasma, Silicone Oil

INTRODUCTION

Droplet-based microfluidics employs either water-in-oil (W/O) or oil-in-water (O/W) emulsions [1]. In general, polydimethylsiloxane (PDMS)-based microfluidic devices are used to generate W/O emulsions, however, its distinct properties, i.e. oil adsorption, gas- and small-molecule permeability and roof collapse are problematic especially in nanochannels. Alternatively, glass-based microfluidic devices can be used after chemical hydrophobization by applying silane solutions, for example perfluorodecyltrichlorosilane (FDTS) or octadecyltrichlorosilane (ODS). However, these chemicals are quite reactive to oxygen or water in air. The modification operation must therefore be skillfully handled under nitrogen atmosphere or in water-free conditions, and even then the procedure often produces debris and imperfectly hydrophobized surfaces, especially in nanochannels or at micro-nanochannel interfaces where the solution can be pinned. Lastly, it is difficult to obtain in-channel hydrophobized patterns with these methods. Here we demonstrate a novel method to modify the glass surface of nanochannels and micro/nanochannel networks.

EXPERIMENTAL

Glass chip was activated by oxygen plasma. Then the micro- and nanochannel network was totally filled with silicone oil. Subsequently the chip was exposed to 265 nm UV light while remaining immersed in the silicone oil to avoid the evaporation of oil. Then, the chip was cleaned by acetone. Optionally, a stainless-steel mask was used to confine hydrophobic patterns on the glass chip upon UV exposure [Fig1]. The modified surface of glass samples were characterized by contact angle measurement and X-ray photoelectron spectroscopy. The stability in different solutions and their usage as a platform to generate W/O emulsions were verified.

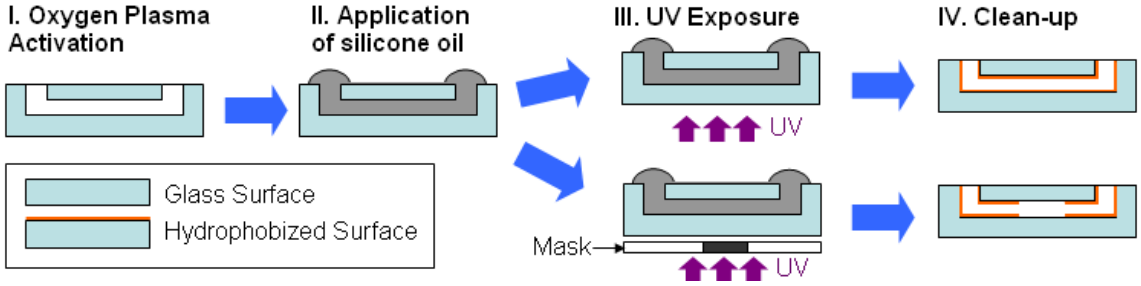

Figure 1: Schematic diagram of the procedure of the surface modification by using oxygen plasma, silicon oil and UV-light.

RESULTS AND DISCUSSION

When the glass chip is exposed to oxygen plasma, plasma can remove contaminants from the glass surface. Furthermore, it can generate Si-O and Si-OH groups on the glass surface [2]. After applying the silicone oil, it will be physically adsorbed to the surface. Upon UV exposure, UV light can break down the silicone oil molecules. Fragments can then immediately react with hydroxyl groups on the glass surface [3] resulting in the hydrophobic surface.

Contact Angle Measurement: Contact angles at the outside of the glass chip were obtained of up to 101° as compared to 30° before modification [Fig 2A]. The effects of oxygen plasma and UV exposure on the surface modification were determined from the change in the contact angle of the outer surface of a glass chip. Table 1 gives a comparison of the contact angle of the glass surface hydrophobized by the different processes (with or without O_2 plasma activation and UV exposure

steps) when applying silicone oil 50 cst in combination with two-hour UV exposure. It was shown that only one step of either oxygen plasma or UV exposure does enhance the contact angle but to a lesser extent than the combination of both steps. Modification of the glass surfaces at different parameters (types of silicon oil and treatment time) were tested to investigate the optimal time for modification [Fig.2B]. Three-hour curing time proved the optimal condition for silicone oil 50 cst since the obtained contact angle was maximum (105.9°). Other types of silicone oil (Silicone Oil 1, 5 and 20 cst) showed the same trend of resultant contact angle as a function of treatment time [Fig.2B]. In addition, stability of the modified surface was investigated by immersing the modified chip into various solutions of different polarity (water, ethanol, acetone, octane, and silicone oil) [Fig.2C]. After 24-hour immersion in different solutions, the contact angles slightly decreased with maximally around 5° indicating the good stability of the hydrophobized surface modified with this approach.

Table 1. Contact angle (degree) of glass surfaces before and after modification using different modification approaches

Before Modification	**After Modification**		
	With O_2 Plasma, With UV exposure	**Without O_2 Plasma, With UV exposure**	**With O_2 Plasma, Without UV exposure**
31.9±3.9	100.9±2.8	68.2±0.2	89.0±4.0

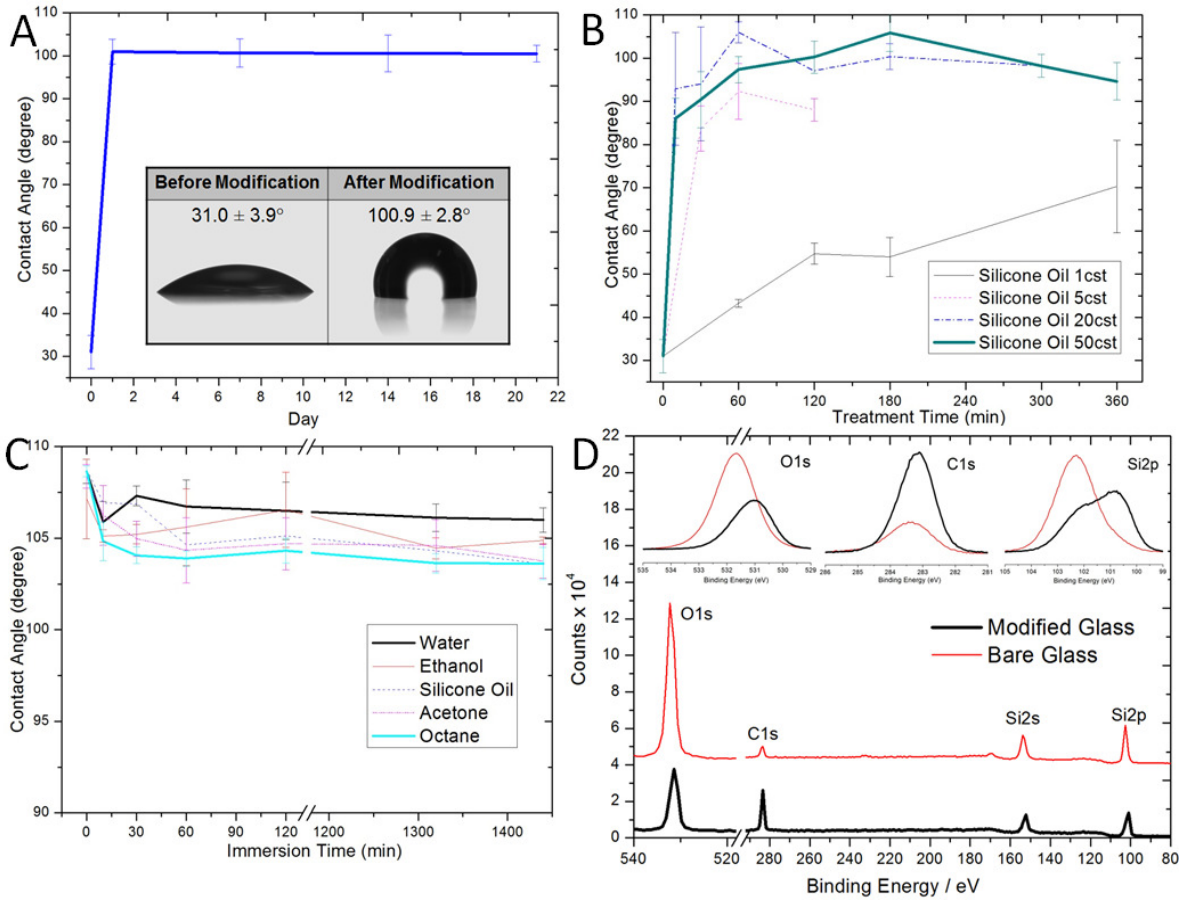

Figure 2: Contact angle measurement of the bare glass surface before and after modification by silicone oil 50 cst till three weeks (A), modification at different UV-treatment time and type of silicone oils (B) and the stability in different solutions until 24 hours (C). (D) XPS data of bare glass and modified glass and the spectra of O1s, C1s and Si1p shown in insets.

XPS Characterization: A XPS survey spectrum of both modified and unmodified samples [Fig. 2D] shows the changes in the atomic ratio of each element, especially for carbon (C1s), oxygen (O1s) and silicon (Si2p). High-resolution spectra of C1s, O1s and Si2p are individually given as insets in Fig. 2D. An obvious increase in carbon atom [Fig.2D inset (C1s)] was attributed mainly to the formation of fragments of silicone oil molecules. The shifts of the binding energy of O1s and Si2p were due to the absence of OH groups and the presence of Si-C or Si-O bonds resulting from the bonding of silicon molecules to the glass surface, respectively [Fig.2D insets (O1s and Si2p)].

In-channel Modified Surface: After modification, no particulate debris appeared inside nanochannels or at intersection of nano- and microchannels [Fig.3A and B]. The inner channels after treatment were hydrophobic and facilitated stable water-in-oil droplet formation in 1-µm-deep channels [Fig 3C]. Homogeneous coating was verified by the continuous flow of generated water droplets in the outlet channels without sticking to the wall [Fig 3D]. This stands in contrast to cases of inhomogeneous coating, where water droplets would become stuck on hydrophilic surface patches. This modified surface was found to be stable during the experimentation for a few hours.

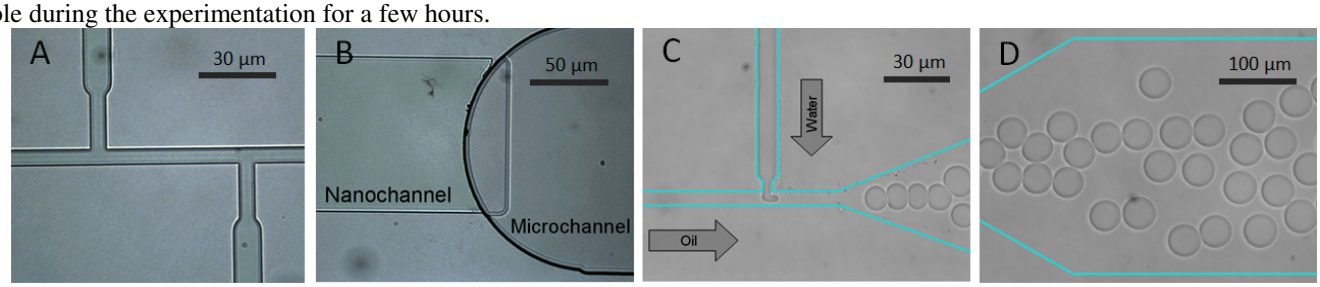

Figure 3: After modification, no particulate debris occurred in nanochannel network (A) or the intersection of nano and microchannel (B). (C) W/O droplet generation in a hydrophobized glass chip (the water phase was DI water and oil phase was 0.5wt% Span 80 in hexadecane solution) and (D) generated W/O droplets flowing in outlet channel without sticking. The depth of nanochannels were 500 nm (Fig.3A and 3B) and 1 µm (Fig.3C and 3D). The depth of all microchannels were 5 µm.

Hydrophobic Patterning: The in-channel hydrophobic patterns were tested by using the principle of hydrophobic valving [4]. Due to the capillary force, water advances in the wetting areas and ceases to advance when reaching the border of the wetting and non-wetting areas. The water will advance through the non-wetting area when an external pressure is given, which is determined by the water/gas interfacial tension (γ_{wg}), the radius of curvature of the aqueous phase relating to the height (h) and the width (w) of the fluidic channel, and the contact angle of the hydrophobic surface (θ_{phob}) [Eq.1]. The hydrostatic pressure of water (P_{hyd}) defined by the height difference of a water reservoir and the microchannel system (ΔH), the density of water (ρ) and the gravitational acceleration (g) was used to provide a relatively low pressure to the water [Eq.2].

$$P_{cap} = 2\gamma_{wg} \cos\theta_{phob} \frac{h+w}{hw} \quad (1)$$

$$P_{hyd} = \rho g \Delta H \quad (2)$$

In our experiment, the height and the width of the fluidic channel were 5 and 100 µm, respectively, the water/air surface tension (γ_{wg}) ≈ 70 mN/m and the height difference (ΔH) was around 35 cm. The applied pressure was therefore approximately 34 mbar, implying a contact angle of the in-channel hydrophobic surface of about 96.4°. This resultant contact angle was slightly lower than the value measured from the outer of glass surface (101°), which we attributed to the fact that the intensity of UV light decreased when transmitted through the 500-µm-thick patterned glass substrate.

CONCLUSION

In summary, a simple technique is presented to hydrophobize glass-based micro and nanofluidic networks that does not significantly generate any particulate debris. Additionally, it is in principle possible to pattern small hydrophobic areas on the glass surface by using a metal mask during UV exposure.

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