Femtosecond Laser-induced Modification in Surface Wettability of PMMA for Microfluidic Applications

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Abstract

Controlled modification of surface wettability of polymethyl methacrylate (PMMA) was achieved by irradiation of PMMA surface with femtosecond (fs) laser pulses. Laser fluences from 0.40 J/cm^2 to 2.1 J/cm^2 produced a hydrophobic surface, whereas fluences from 2.1 J/cm^2 to 52.7 J/cm^2 (maximum investigated) produced a hydrophilic surface. Fluences less than 0.31 J/cm^2 had no effect on the wettability of the raw PMMA. Microchannels fabricated using fs laser can have tailored surface wetting characteristics for controlling the liquid flow resistance, and thus controlling the liquid sample separation ratio in different channels. A concave flowing front was observed in a microchannel with hydrophilic surface. Correspondingly, a convex flowing front was observed with hydrophobic surface. For a untreated channel, a straight flowing front was observed. These results offer greater possibilities in microfluidic chip design with surfaces of controlled hydrophobic and hydrophilic properties.

1 Introduction

The surface wettability determines the reagent flowing behaviour in different microchannels, and the ease of adhesion of cells on polymeric surfaces [1]. Modification of PMMA surface wettability is highly desirable as PMMA is commonly used in various microfluidic devices [2]. Laser irradiation is one promising method for such ends [3]. Long wavelength cw CO_2 (10.6 μm) and millisecond Nd:YAG (1.06 μm) lasers result in a mainly photothermal process, and thus little effect in PMMA surface wettability [4]. In contrast, the shorter wavelength (248 nm) UV excimer laser has high photon energy; in addition to photothermal effect, it causes photochemical decomposition and thus a reduction in water contact angle (WCA) from 76º for the raw PMMA surface to 25º [5]. As ultrashort laser pulses have ultrahigh peak power resulting in a nonliner absorption mechanism with little photothermal effect [6], different surface modification phenomenon can be expected. Thus, we explore here the wettability modification with fs laser pulses for microfluidic applications.

2 Experimental

Commercially available 1 mm thick PMMA substrate was irradiated by a fs laser (CPA2001 Clark-MXR, wavelength 775 nm). At 1 kHz repetition rate and 300 mW attenuated power, the laser beam was focused by a conventional focusing lens (focal length of 100 mm). Through a galvanometer scanner, 5 mm by 5 mm surface area was horizontally raster-scanned at a shifting pitch of 25 µm. The scanning speed was 2 mm/s. Surface was modified with various laser fluences by adjusting the defocusing distance *Z*, with positive or negative *Z* indicating that the focal plane is above or below respectively the sample surface. To characterize surface wettability, WCA (variation within ±1º) was measured in room temperature and ambient air conditions (relative humidity 60%) using VCA Optima XE, by releasing a 0.5 µl droplet onto the surface.

3 Results and disussion

3.1 Wettability modification by laser irradiation

Figure 1 is a plot of WCA of the irradiated surface and the laser fluence against the defocusing distance *Z*. When the sample surface was on the laser focal plane, water droplet spread rapidly across the surface with boundary beyond the field of view of the microscope. Thus, WCA was deduced to approach 0º, indicating super-hydrophilicity. WCA increased with increasing magnitude of defocusing distance, indicating a decrease of surface hydrophilicity. With *Z* more than 3 mm, WCA exceeded 90º, indicating a hydrophobic surface. Maximum WCA of approximately 125º was achieved for *Z* of 7 mm. For *Z* greater than 8 mm, WCA decreased to 76-78º, which was similar to that of a raw PMMA surface. Figure 1 shows the symmetry of WCA with respect to *Z*, i.e. similar WCA value for the same *Z*. For a given laser power, the same *Z* will have the same laser fluence, indicating that laser fluence is the key determining factor of WCA. The change in WCA over the range of fluence investigated was significant. Near zero degree in WCA was achieved at high fluence of 52.7 J/cm^2 (Z of 0 mm), and 125° at a fluence of 0.40 J/cm^2 (Z of 7 mm). Fluencies below 0.31 J/cm^2 (Z of 8 mm or more) remained WCA similar to that of the raw PMMA surface, indicating the level of fluence was below the threshold to cause any noticeable changes to the PMMA surface.

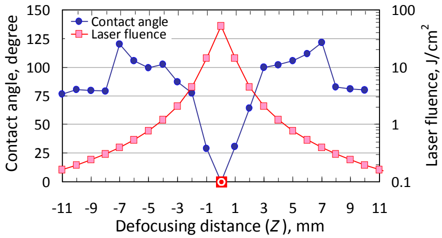

Figure 1: Effect of defocusing distance Z on water contact angle (WCA).

X-ray photoelectron spectroscopy analysis (O1s and C1s) showed that more polar groups such as O−C and O=C were produced at high fluences, and thus increased hydrophilicity, inversely, decreased hydrophilicity. The level of fluences determines the degree and nature of photodegradation, which dictates the level of wettability.

3.2 Sample separation in microchannels

A Y-chip was fabricated by fs laser direct writing on a PMMA substrate. One of the two branch channels was written at low laser fluences to achieve a hydrophobic or low hydrophilic channel surface, while the other channel was written at high fluences for highly hydrophilic surface. The PMMA substrate was bonded with a PDMS substrate by mechanical pressure without the use of glue at room temperature, and thus to avoid possible contamination. When water was injected into the Y-chip channels using a syringe, the varied flowing velocity in the two channels was clearly observed as shown in figure 2. The velocity ratio of in the two branches was calculated from the flowing distance to be 3.3 for highly hydrophilic channel to low hydrophilic channel (top row, Fig. 2) and 13.7 for highly hydrophilic channel to hydrophobic channel (bottom row, Fig. 2). Thus, surface wettability affects the flowing resistance, and the separation ratio of liquid in different microchannels could be controlled by varied channel surface wettability.

To understand the natural flowing behaviour without external driving force, a standard Y-mixer was fabricated by fs laser on PMMA and then thermally bonded with another PMMA plate at 4.3 MPa and 106 °C for 20 mins. After injection of water into the channel, it was observed that a concave flowing front appeared on the super hydrophilic surface, a convex flowing front on the hydrophobic surface, and a straight flowing front on the raw surface (Fig. 3).

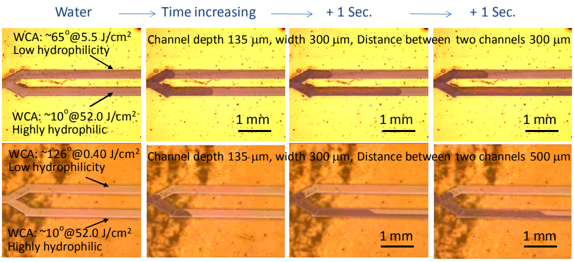

Figure 2: Effect of surface wettability on flowing behaviour in microfluidic channels.

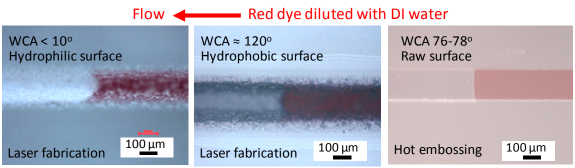

Figure 3 Water flowing front in microchannels with controlled surface wettability

4 Conclusions

Modification of PMMA surface wettability to be hydrophilic or hydrophobic over a wide range of water contact angle for microfluidic applications was achieved by flexible irradiation of PMMA surface with various fs laser fluences.

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