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## Surface Wettability Modification of Cyclic Olefin Polymer by Direct Femtosecond Laser Irradiation

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**Abstract:** The effect of laser irradiation on surface wettability of cyclic olefin polymer (COP) was investigated. Under different laser parameters, a superhydrophilic or a superhydrophobic COP surface with a water contact angle (WCA) of almost 0° or 163°, respectively, could be achieved by direct femtosecond laser irradiation. The laser power deposition rate (PDR) was found to be a key factor on the wettability of the laser-treated COP surface. The surface roughness and surface chemistry of the laser-irradiated samples were characterized by surface profilometer and X-ray photoelectron spectroscopy, respectively; they were found to be responsible for the changes of the laser-induced surface wettability. The mechanisms involved in the laser surface wettability modification process were discussed.

**Keywords:** femtosecond pulsed laser; laser power deposition rate (PDR); cyclic olefin polymer (COP); wettability; surface modification

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## 1. Introduction

The controlled modification of polymer surface wettability to either hydrophilic or hydrophobic is highly desirable for various applications. For example, super-hydrophobic surfaces are well suited for the self-cleaning of contaminants. Surface wettability also determines the reagent flow behavior in microfluidic channels, and the ease of adhesion of cells. A highly hydrophilic surface can improve surface adhesion and wettability, a desirable characteristic for coating and joining applications. High wettability contrast surfaces could confine inkjet droplets to the hydrophilic region and avoid the hydrophobic region, with the potential of a printed line-width less than the droplet diameter. Indeed, the surface modification of polymer materials has been widely investigated recently [1–4]. Cyclic olefin polymer (COP) is one of the widely used polymers in microfluidics and biotechnologies. The controlled modification of COP surface wettability is highly desirable for the fabrication of COP-based microfluidic devices. Different techniques can be employed to modify polymer surface wettability which include wet-chemical etching [5], corona discharges [6], plasma treatment [7,8], ion beam treatment [9,10], electron beam irradiation [11], and laser irradiation. Compared with other methods, laser irradiation, being a fast and clean process, has a number of unique advantages. It is a non-contact and highly selective process. It can provide localized treatment and precise control for producing complex features with minimal thermal effect on the bulk material. Laser irradiation has been applied for surface modification of metals, polymers, and semiconductors [4,12–17]. Ultrashort pulsed lasers are increasingly used as a tool for surface treatment. In contrast to long pulsed lasers, ultrashort pulsed lasers can induce nonlinear absorption of photons and have minimum thermal effect. In addition, the use of ultrashort femtosecond laser pulses allows treatment of features with micrometric precision, as the laser beam can be accurately positioned and tightly focused into a spot size of several microns. In this investigation, we demonstrated that an infrared femtosecond laser can induce both superhydrophobicity (WCA of  $163^\circ$ ) and superhydrophilicity (WCA of almost  $0^\circ$ ) on COP material surface through direct laser irradiation under different laser parameters. The effects of laser fluence, power deposition rate, and surface roughness on the COP surface's wettability were investigated. This developed process has potential applications for the fabrication of polymer microfluidic devices or to generate high wettability contrast surfaces for inkjet printing.

## 2. Experiments

A COP sheet with a thickness of 2 mm from ZEON Corporation (Tokyo, Japan) was used in the experiments. The COP samples were treated with a femtosecond (fs) laser beam. The fs laser system is based on a regenerative Ti:Sapphire amplifier using chirped pulse amplification technique (CPA 2001, Clark-MXR, Inc., Dexter, MI, USA) which provides high-intensity fs laser pulses. The pulse duration of the output beam from the amplifier is 150 fs with a nominal wavelength of 775 nm. The repetition rate is 1000 Hz and the beam profile emitted from the regenerative amplifier is approximately Gaussian. The average output power can reach 800 mW at a repetition rate of 1000 Hz. The sample was placed on a stationary stage and the laser beam was deflected by a Scanlab galvanometer scanner for scanning treatment of the sample surface. The focused beam spot size was measured to be around 30  $\mu\text{m}$  in diameter on the sample surface. The COP sample surface was treated under different laser

fluences and power deposition rates. The morphology of the laser-treated samples was analyzed using scanning electron microscopy (SEM) (5600LV, Jeol Asia Pte Ltd., Tokyo, Japan), X-ray photoelectron spectroscopy (XPS) (VG ESCALAB 220i-XL, Thermo Scientific, East Grinstead, West Sussex, UK), and surface profilometry (NANOVEA PS50, Nanovea, Irvine, CA, USA). The surface water contact angle (WCA) was determined by the sessile drop method with VCA Optima (VCA-2500XE AST Products, Inc., Billerica, MA, USA) using 1  $\mu$ L de-ionized water droplet. The drop was formed from a capillary tip of a syringe, and was detached gently from the tip onto the substrate. The VCA Optima utilizes a precision camera and advanced PC technology to capture the image of the droplet and determine tangent line for the contact angle measurement. The WCA measurement was conducted in room temperature around 21 °C (relative humidity 60%) with variation within  $\pm 2^\circ$ . The average value based on three measurements per laser parameter on different areas was obtained. Contact angle was measured directly after laser treatment.

### 3. Experimental Results and Discussion

To investigate the wettability change induced by fs laser treatment under different laser conditions, the COP substrates were treated with a number of different laser fluences from 17.6 to 30.79 J/cm<sup>2</sup>. Fluence is the average energy deposited per unit area on the sample surface by a single pulse [18], which is calculated as:

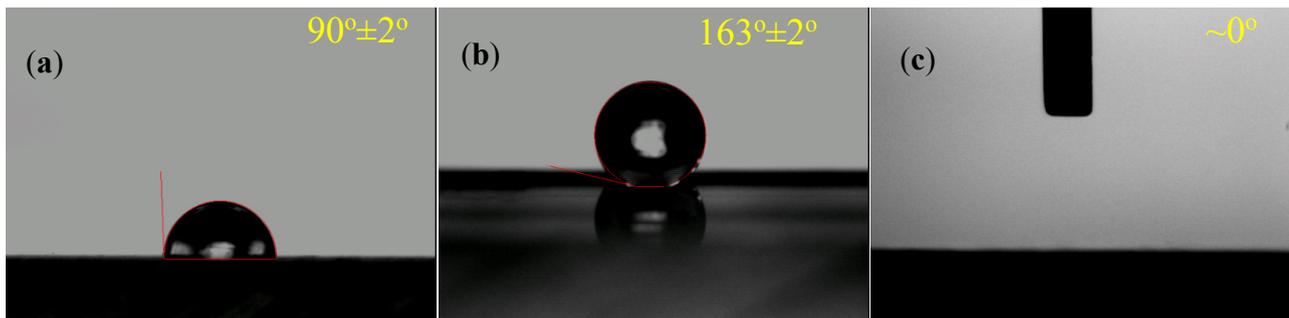
$$F = \frac{E_{pulse}}{A} \quad (1)$$

where  $E_{pulse}$  is the pulse energy and  $A$  is the spot area.

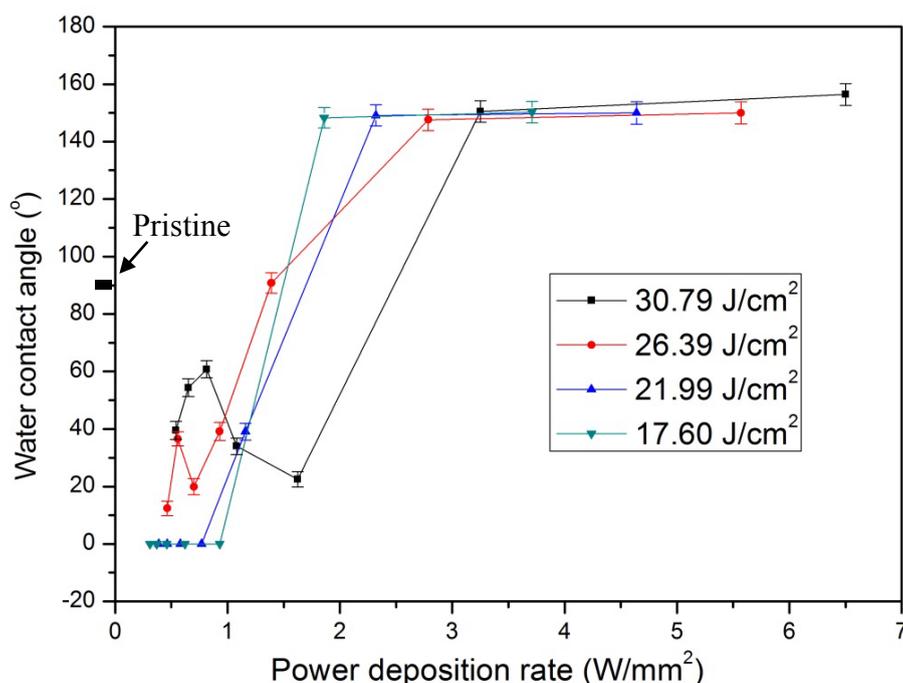
For a line scan of the laser beam, the power deposition rate (PDR) is an appropriate parameter to be considered, which is defined as the energy deposited on the sample surface per unit time per unit area [18]. PDR can be calculated as:

$$PDR = \frac{E_{pulse} \cdot RR}{D \cdot SS} \quad (2)$$

where  $RR$  is the laser repetition rate (fixed at 1 kHz in this investigation),  $D$  is the scanning width equal to the laser spot diameter on the surface, and  $SS$  represents the scanning speed. Overlapped multiple scans are required to modify the wettability of an area [19]. In this investigation, the shifting pitch was fixed at 0.02 mm. It was found that the WCA varies with the fluence and power deposition rate. With the appropriate laser conditions, the surface wettability of COP could be tuned from superhydrophobic to superhydrophilic as shown in Figure 1. When the COP surface was treated at a high fluence of 30.79 J/cm<sup>2</sup> and a high PDR of 6.5 W/mm<sup>2</sup>, the WCA was increased to around 163° from the original 90°, as shown in Figure 1b. In contrast, when the COP surface was treated at a low fluence of 17.60 J/cm<sup>2</sup> and a low PDR of 0.62 W/mm<sup>2</sup>, the WCA was decreased from the original 90° to almost zero degrees, as shown in Figure 1c. Furthermore, as shown in Figure 2, when the laser fluence was fixed at a constant fluence, with decreasing PDR, the WCA decreased to less than 40° from the original 90°. These findings indicated that the power deposition rate is a key factor in determining the wettability of the laser-treated COP surface. The WCA could be tuned from superhydrophobic to superhydrophilic by adjusting PDR via controlling the laser pulse energy and the beam scanning speed.



**Figure 1.** Water contact angle of (a) pristine cyclic olefin polymer (COP) surface; (b) COP surface treated with fluence of  $30.79 \text{ J/cm}^2$  and power deposition rate (PDR) of  $6.5 \text{ W/mm}^2$ ; and (c) COP surface treated with fluence of  $17.60 \text{ J/cm}^2$  and PDR of  $0.62 \text{ W/mm}^2$ .



**Figure 2.** Effect of power deposition rate on water contact angle at different fluence.

It is well known that surface wettability is governed by surface morphology and surface chemistry [13]. As such, the laser-induced surface wettability changes may be due to changes in surface roughness and/or surface chemistry.

There are two existing theories for describing the effect of surface roughness on wettability. The first theory by Wenzel [20] assumes that liquid fills the whole area of the rough surface. The relationship between the macroscopic contact angle and the equilibrium contact angle may be written as:

$$\cos \theta_m = r \cdot \cos \theta_s \quad (3)$$

where  $\theta_m$  and  $\theta_s$  are, respectively, the measured contact angle on a structured surface and the equilibrium contact angle on an ideally smooth surface; the roughness factor  $r$  is the ratio of the actual rough surface area to the geometrically projected area.

Assume that the contact angle is more than  $90^\circ$  on a smooth surface. If a micro- or nano-pattern is fabricated on this smooth surface, its hydrophobic characteristic will be enhanced. The same analogy applies to a hydrophilic surface. For example, for a smooth surface with a contact angle less than  $90^\circ$ , a micro- or nano-pattern fabricated on this smooth surface will enhance its hydrophilic characteristic.  $r$  should increase closer to 1, and  $\theta_m$  should increase for a hydrophobic surface and decrease for a hydrophilic surface.

The second theory by Cassie and Baxter [21] assumes that the liquid does not completely wet the roughened substrate. The relationship between the macroscopic contact angle and the equilibrium contact angle may be written as:

$$\cos \theta_m = \varphi \cdot \cos \theta_s + \varphi - 1 \quad (4)$$

where  $\varphi$  is the fraction of wetted surface area divided by its projected area. If a surface is rough enough so that air may be entrapped between the liquid and the solid, the interface becomes composite and the contact angle increases with the roughness even if the surface chemistry is intrinsically hydrophilic.

Figure 3 shows the measured surface morphologies of the laser-treated and pristine COP surfaces at different PDRs with a fixed fluence of  $26.39 \text{ J/cm}^2$ . Ablation occurred on all samples. When the COP substrate was treated at a high PDR of  $5.57 \text{ W/mm}^2$ , a superhydrophobic surface was obtained. The surface became rougher and micro-groove patterns were formed on the surface, as in Figure 3b. In contrast, when the COP surface was treated at a low PDR such as  $0.93 \text{ W/mm}^2$ , a hydrophilic surface was obtained. The surface became slightly rougher but was still quite consistently smooth with no grooved patterns formed, as shown in Figure 3e. Figure 4 shows the change of the measured water contact angles of laser-treated COP surfaces as a function of surface roughness. Here, the laser treatment was conducted at fluences of  $30.79 \text{ J/cm}^2$ ,  $26.39 \text{ J/cm}^2$ ,  $21.99 \text{ J/cm}^2$ , and  $17.60 \text{ J/cm}^2$  with different PDRs from  $0.31 \text{ W/mm}^2$  to  $6.5 \text{ W/mm}^2$ , as shown in Figure 2. The surface roughness ( $Ra$ ) was measured by a one-dimensional roughness scan perpendicular to the laser scanning direction. The scanning length was 5 mm. It can be observed that the water contact angle increased from about  $90^\circ$  for the pristine COP surface to almost  $150^\circ$  with an increase in the surface roughness. In contrast, when the substrate was treated at a lower PDR, the induced surface roughness was in the range of  $1.0$  to  $2.5 \mu\text{m}$ , and the water contact angle decreased from  $90^\circ$  for the pristine COP surface to almost  $0^\circ$  for laser-treated surfaces. The effect of PDR on surface roughness is depicted in Figure 5.

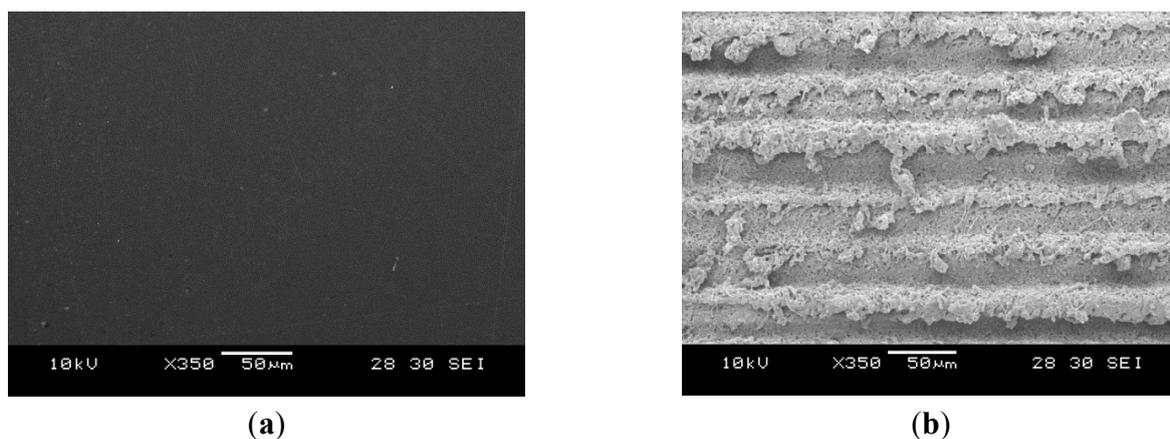
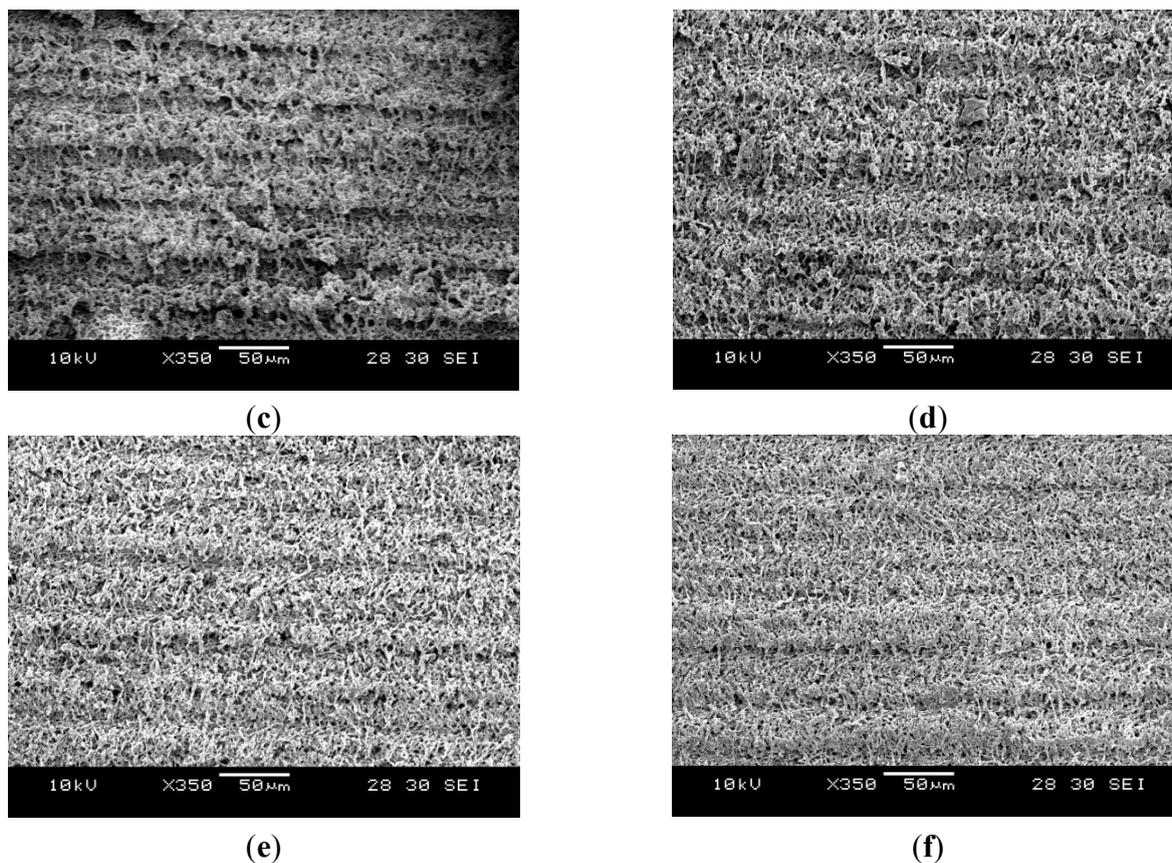
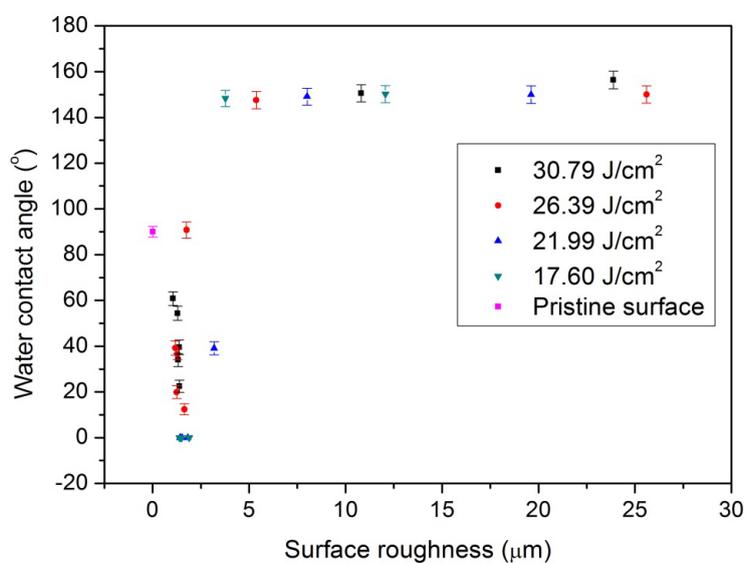


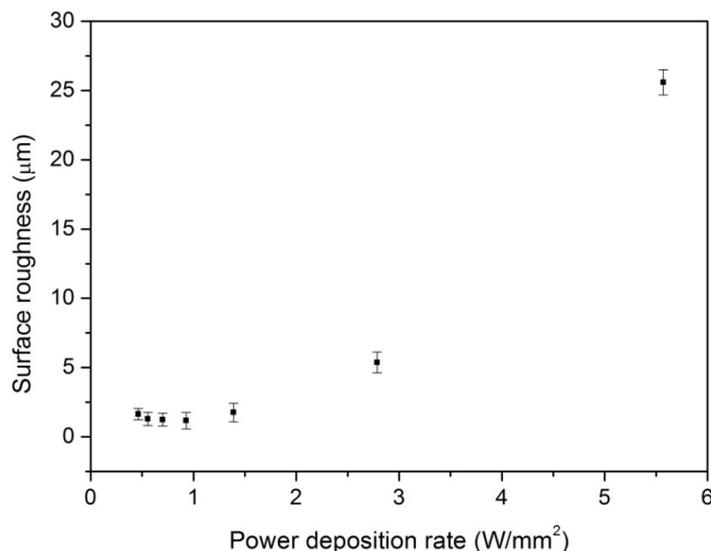
Figure 3. Cont.



**Figure 3.** Scanning electron microscopy (SEM) images of surface morphologies at different PDRs with laser fluence fixed at  $26.39 \text{ J/cm}^2$ . (a) Pristine COP surface; (b) PDR:  $5.57 \text{ W/mm}^2$ ; (c) PDR:  $2.79 \text{ W/mm}^2$ ; (d) PDR:  $1.39 \text{ W/mm}^2$ ; (e) PDR:  $0.93 \text{ W/mm}^2$ ; (f) PDR:  $0.7 \text{ W/mm}^2$ .



**Figure 4.** Water contact angle as a function of surface roughness of pristine surface and laser-treated surfaces with various different roughnesses. Here, the laser treatment was conducted at fluences of  $30.79 \text{ J/cm}^2$ ,  $26.39 \text{ J/cm}^2$ ,  $21.99 \text{ J/cm}^2$ , and  $17.60 \text{ J/cm}^2$  with different PDRs from  $0.31 \text{ W/mm}^2$  to  $6.5 \text{ W/mm}^2$  as shown in Figure 2.



**Figure 5.** Effect of PDR on surface roughness at a fixed laser fluence of 26.39 J/cm<sup>2</sup>.

Based on the experimental observations and Wenzel and Cassie and Baxter theories, the formation of the superhydrophobic surfaces treated with higher laser PDR are believed to be mainly due to the increase of the surface roughness, leading air to become entrapped between the liquid and the solid; the interface becomes composite and the contact angle increases with roughness.

For COP substrates treated under lower laser PDR, the formation of the hydrophilic surfaces is most possibly due to the laser-induced change of the surface chemistry instead of the surface roughness. It is known that the water contact angle of pristine COP is around 90°. Based on the Wenzel or Cassie and Baxter theories, the water contact angle will increase with an increase of surface roughness for this inherently hydrophobic material. However, when the surface roughness was increased from that of the original surface ( $Ra = 7.98$  nm) to an  $Ra$  of 2.5 μm, almost 0° superhydrophilic surface was achieved as shown in Figure 1c. Thus, the laser-induced change in surface chemistry must play a key role in the formation of the superhydrophilic COP surfaces.

It is known that oxygen-containing groups on a polymer surface, such as C–O, C=O, and O–C=O, are responsible for the change of surface hydrophilicity [22]. As the polarity of the C=O bond is more intense than that of the C–O bond, the C=O double bond is most important for the hydrophilicity of polymer surfaces. To fully understand the changes in surface wettability induced by laser irradiation, X-ray photoelectron spectroscopy (XPS) analysis using a VG ESCALAB 220i-XL was employed to identify the chemical bonds. Monochromatic Al K $\alpha$  X-ray ( $h\nu = 1486.7$  eV) was employed for XPS analysis with a photoelectron take-off angle of 90° with respect to the surface plane. The analysis area was approximately 700 μm in diameter with the maximum analysis depth in the range of 4–8 nm. The resolution of binding energy is estimated to be within  $\pm 0.2$  eV. The measured C1s spectra of pristine and laser-treated samples at a PDR of 2.79 W/mm<sup>2</sup> were shown in Figure 6. The main peak at around 285.0 eV was the C–H or C–C bond, while the sub-peaks at 286.3 eV and 288.6 eV were attributed to the C–O bond and C=O bond, respectively [7]. In the XPS measurements, the analysis area is approximately 700 μm in diameter, which is much larger than the laser-induced micro-feature dimensions of around 50 μm. The XPS signal is an average value for the whole analyzed surface area, which should be reliable to illustrate the changes between the original surface and the laser-treated

surfaces under different laser parameters, even if the surface roughness (several micrometers) is much larger than the XPS information depth of about a few nm [23,24]. Oxygen concentration or polar groups increased on the surface after laser treatment as shown in Table 1. This increase in oxygen polar groups on the COP surface led to an increase in wettability; this could result in a highly hydrophilic surface. For a laser-induced superhydrophobic surface treated with a fluence of  $26.39 \text{ J/cm}^2$  and a PDR of  $5.57 \text{ W/mm}^2$ , although the oxygen content also increased slightly, the roughness of the surface increased significantly ( $R_a$  of  $25.6 \text{ }\mu\text{m}$ ) with the formation of micro-ripple structures as shown in Figure 3b. Thus, air might be entrapped between the liquid and the solid; the interface became composite and the contact angle increased to more than  $150^\circ$  even if the surface had some oxygen polar groups. The WCA decreased to hydrophilic at lower a PDR compared with pristine COP. The WCA is significantly influenced by surface structure when the surface is rough. In contrast, the influence of surface chemistry on the WCA is significant when the surface is relatively smooth ( $R_a$  less than  $1.76 \text{ }\mu\text{m}$ ).

The time dependency of the WCA of a laser-modified surface, especially for a laser-induced hydrophilic surface, was observed. The laser-modified hydrophilic or even superhydrophilic surface is not stable, in that the surface could recover to hydrophobic after a period of time subsequent to laser treatment. This recovery of the WCA over time is currently being investigated.

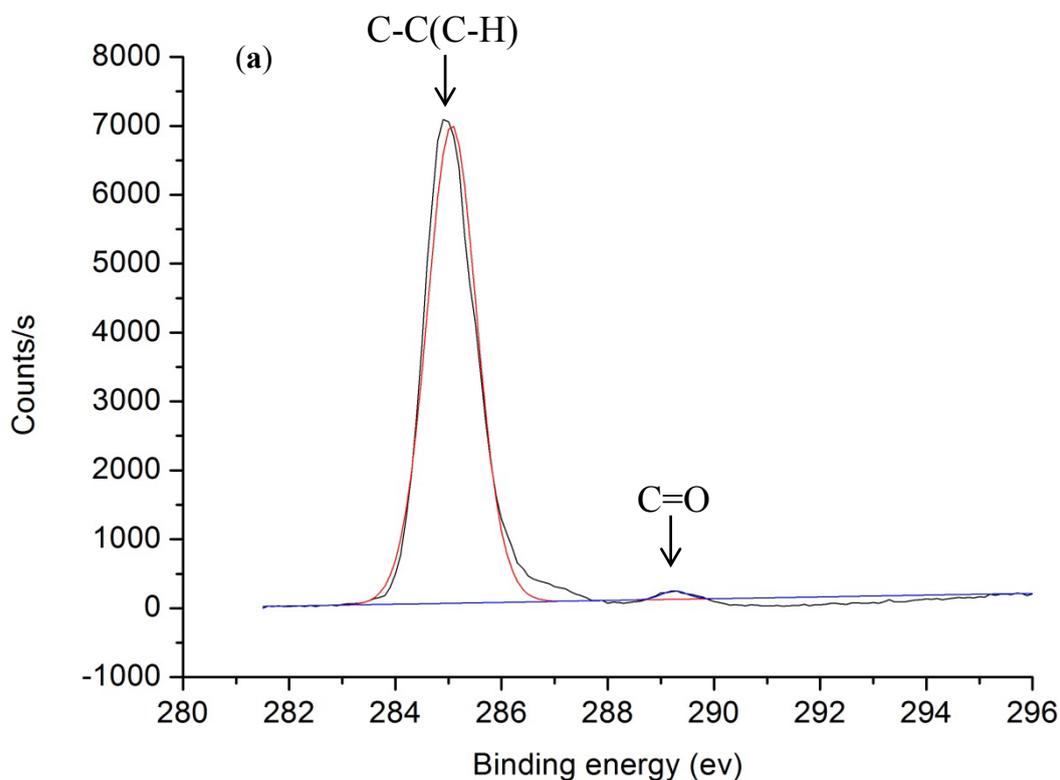
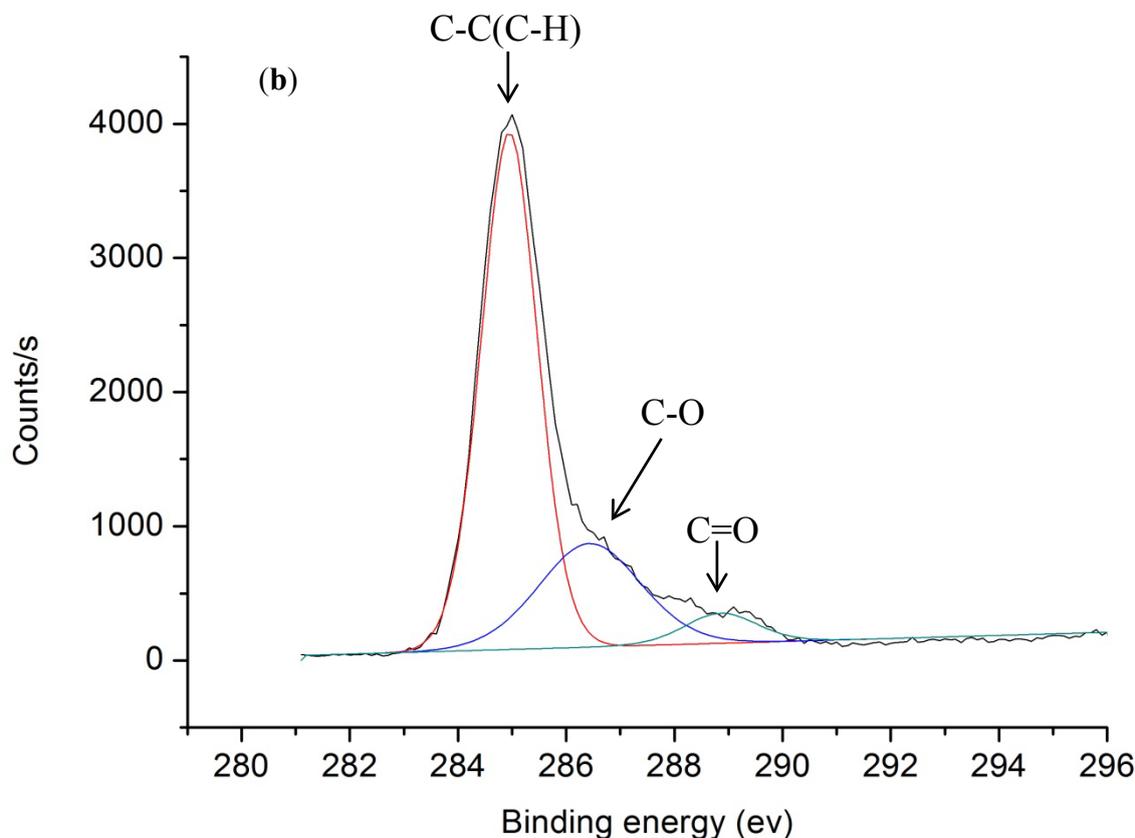


Figure 6. Cont.



**Figure 6.** X-ray photoelectron spectroscopy (XPS) spectra of (a) pristine COP surface and (b) COP surface treated with a PDR of 2.79 W/mm<sup>2</sup> at a fixed fluence of 26.39 J/cm<sup>2</sup>.

**Table 1.** Polar and non-polar groups formed on the COP surface before and after laser treatment at a fixed laser fluence of 26.39 J/cm<sup>2</sup>.

| PDR<br>(W/mm <sup>2</sup> ) | Non-polar Groups<br>C-C/C-H (at. %) | Polar Group<br>C-O (at. %) | Polar Group<br>C=O (at. %) | Sum of Polar<br>Groups (at. %) | Overall Ratio of<br>Polar and Non-<br>Polar Groups | Water<br>Contact<br>Angle |
|-----------------------------|-------------------------------------|----------------------------|----------------------------|--------------------------------|--|---------------------------|
| 0                           | 98.35                               | -                          | 1.65                       | 1.65                           | 0.02   | 90.0°                     |
| 5.57                        | 75.03                               | 19.11                      | 5.85                       | 24.96                          | 0.33   | 150°                      |
| 2.79                        | 71.05                               | 23.22                      | 5.72                       | 28.94                          | 0.41   | 147.55°                   |
| 1.39                        | 62.33                               | 31.52                      | 6.14                       | 37.66                          | 0.60   | 90.8°                     |
| 0.93                        | 70.96                               | 20.98                      | 8.04                       | 29.02                          | 0.41   | 39.2°                     |
| 0.70                        | 59.32                               | 34.71                      | 5.95                       | 40.66                          | 0.69   | 19.9°                     |
| 0.56                        | 71.44                               | 20.37                      | 8.17                       | 28.54                          | 0.40   | 36.6°                     |

#### 4. Conclusions

The effects of laser irradiation on surface wettability of COP were investigated. It was demonstrated that a superhydrophilic COP surface with a water contact angle of almost 0° and a superhydrophobic COP surface with a water contact angle of 163° could be achieved by direct fs laser irradiation with different laser parameters. The laser power deposition rate was found to be a key factor in determining the wettability of the laser-treated COP surface. The surface roughness of the laser-irradiated samples was found to be responsible for the changes of the laser-induced surface wettability at a high laser power deposition rate; in contrast, the laser-induced change in surface chemistry was a key factor in

determining the wettability change for the COP substrates treated at low laser power deposition rates. The developed process could be applied for the controlled modification of localized surface wettability of microfluidic devices or the formation of high wettability contrast surfaces for inkjet printing.

### Supplementary Materials

Supplementary materials can be accessed at: <http://www.mdpi.com/2079-4991/5/3/1442/s1>.

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### Author Contributions

Bing Wang contributed to the major laser processing work, characterization and measurement, data analysis and manuscript drafting. Xincai Wang contributed to experimental data discussion and manuscript revision. Yee Cheong Lam provided guidance on the experimental work and finalizing the manuscript. Hongyu Zheng contributed to the project discussion.

### Conflicts of Interest

The authors declare no conflict of interest.

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