

## Femtosecond laser-induced surface wettability modification of polystyrene surface

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In this paper, we demonstrated a simple method to create either a hydrophilic or hydrophobic surface. With femtosecond laser irradiation at different laser parameters, the water contact angle (WCA) on polystyrene's surface can be modified to either 12.7° or 156.2° from its original WCA of 88.2°. With properly spaced micro-pits created, the surface became hydrophilic probably due to the spread of the water droplets into the micro-pits. While with properly spaced micro-grooves created, the surface became rough and more hydrophobic. We investigated the effect of laser parameters on WCAs and analyzed the laser-treated surface roughness, profiles and chemical bonds by surface profilometer, scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS). For the laser-treated surface with low roughness, the polar (such as C—O, C=O, and O—C=O bonds) and non-polar (such as C—C or C—H bonds) groups were found to be responsible for the wettability changes. While for a rough surface, the surface roughness or the surface topography structure played a more significant role in the changes of the surface WCA. The mechanisms involved in the laser surface wettability modification process were discussed.

**femtosecond laser, polystyrene (PS), wettability, micro-pits & micro-grooves, surface texturing and surface modification**

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### 1 Introduction

The controlled surface wettability modification of polymers is exceedingly alluring for different applications. For example, the surface adhesion and wettability can be improved with a hydrophilic surface, which is suitable for joining and coating applications. The wettability can also help to control the reagent flow in a microfluidic channel. A low hysteresis superhydrophobic surface has a self-cleaning or anti-contamination property. Recently, the surface modification of polymers has been widely investigated [1-4]. Polystyrene

(PS) is one of the most generally used polymers in microfluidics and biotechnology applications. Different techniques including ion beam treatment [5,6], plasma treatment [7,8], electron beam irradiation [9], wet-chemical etching [10], corona discharges [11] and laser irradiation have been applied for the surface wettability modifications. Compared with other treatment techniques, laser irradiation is a relatively fast, simple and cost-effective method. Recently, femtosecond laser (fs) is increasingly used for surface modification due to its high precision, ultra-short pulse duration and high laser power intensity. Different types of materials including semiconductors, metals and polymers [12-18] have been treated by fs laser irradiation. In this paper, we demonstrated that PS surface can be tuned to

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either highly hydrophilic or superhydrophobic with the fs laser irradiation. The effect of laser parameters on surface microstructures and surface WCAs has been investigated.

## 2 Materials and method

Commercially available PS sheets (1.2 mm thick) were used in the experiments. A Ti: Sapphire based Quantronix Integra-C femtosecond laser with pulse duration of 130 fs was used for the surface treatment. The laser central wavelength is 795 nm. The repetition rate was fixed at 1 kHz and the maximum output laser power was 1.5 W. The laser beam was focused onto the sample surface through Scanlab galvanometer scanners. The focal spot diameter was around 30  $\mu\text{m}$ . The beam profile was approximately Gaussian. The laser processing experiments were conducted in an ambient air environment. The room temperature was around 21°C and relative humidity was around 60%. The PS sample surface was treated under different laser fluence and scanning speeds. The surface properties after laser treatment were analyzed using scanning electron microscope (SEM) (5600LV, Jeol Asia Pte Ltd., Japan), surface profilometer (NANOVEA PS50, Nanovea, USA) and X-ray photoelectron spectroscopy (XPS) (ESCALAB 250Xi, Thermo Scientific, UK). The surface WCA measurement was conducted by applying the sessile drop method. A VCA optima (VCA-2500XE AST Products, Inc. USA) was used for the water contact angle measurement with a fixed water droplet volume of 1  $\mu\text{L}$ .

## 3 Experimental results and discussion

### 3.1 Hydrophilic modification

In order to modify the PS surface to be more hydrophilic or more hydrophobic, different surface patterns were created on the sample surface under different laser parameters. To increase the hydrophilicity, a matrix of micro-pits with the center spacing between two micro-pits of 200  $\mu\text{m}$  was created on the surface. It was observed that the water droplets easily spread into micro-pits created, which enabled the surface to be more hydrophilic. The effect of laser fluence on the WCA was depicted in Figures 1 and 2 in our previous publication [19]. A highly hydrophilic surface (WCA of 12.7°) was obtained when the laser fluence was at about 193.9 J/cm<sup>2</sup>. The SEM image showing the micro-pits created by laser ablation was shown in Figure 3(b). We have reported in our previous publication [19] that the surface structures (depth, size and density of the created micro-pits) had significant effect on the surface wettability, which increased with increasing the depth, size, or density of the micro-pit matrix. This was consistent with Wenzel's model [20].

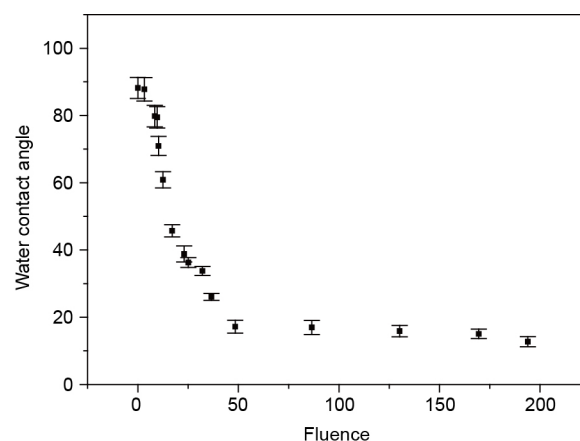


Figure 1 Surface water contact angle at different laser fluence [19].

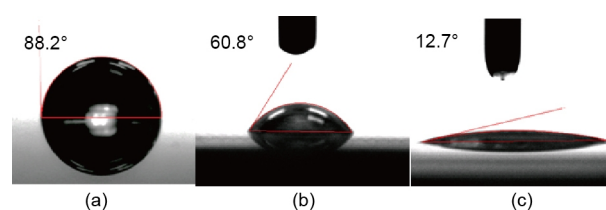


Figure 2 (Color online) Water contact angle of a pristine sample surface (a), surface treated at a fluence of 12.5 J/cm<sup>2</sup> (b) and surface treated at a fluence of 193.9 J/cm<sup>2</sup> (c).

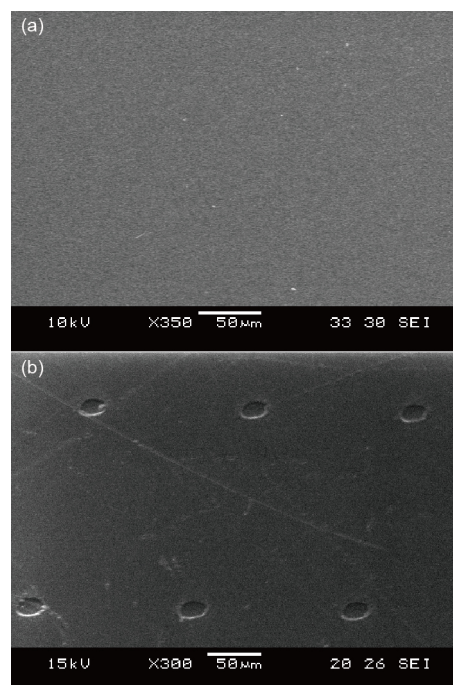


Figure 3 SEM image of pristine sample surface (a) and micro-scale pits created on the sample surface after laser treatment (b).

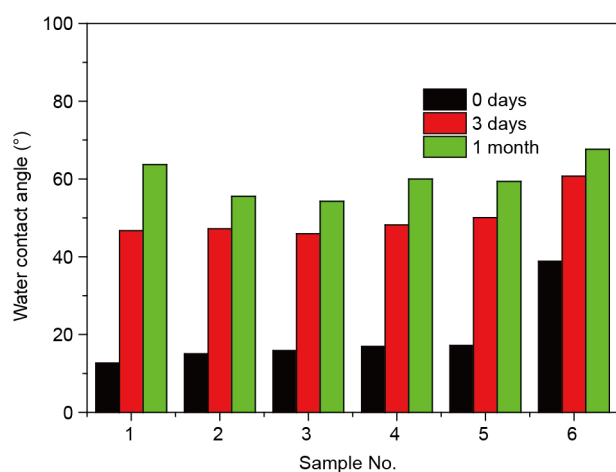
The WCAs of a hydrophilic surface tend to restore its original untreated value over time in the open-air environment after the surface being treated with different methods including

laser irradiation, chemical treatment, and plasma treatment. It can happen within a few hours to few weeks depending on the materials, treatment methods, treatment parameters and storage environment [21]. The WCA recovery may be due to reaction between the treated surface and air. Figure 4 showed the WCA of laser treated samples over time. As time increased, the WCA tends to recover to its original value.

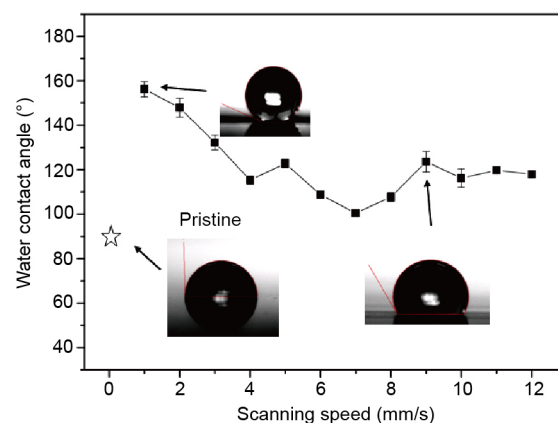
### 3.2 Hydrophobic modification

In order to create a hydrophobic surface on the initially hydrophilic material such as PS, the surface needs to have a certain roughness for air to be trapped in the gap between the sample surface and water droplets [22]. In our work, micro-scale grooves were created on the sample surface at different laser parameters. A 3 mm × 3 mm surface area was scanned with the scanning speed varied from 1 to 12 mm/s. The fluence was fixed at 5.66 J/cm<sup>2</sup> with a shifting pitch of 200 μm. The effect of scanning speed, which determines the number of pulses on each irradiated location, on the surface WCA was shown in Figure 5. It can be seen that the sample surface was modified into superhydrophobic (WCA of 156.2°) from original 88.2° at a scanning speed of 1 mm/s. Figure 6 showed the SEM images of the sample surface structure irradiated under different scanning speeds.

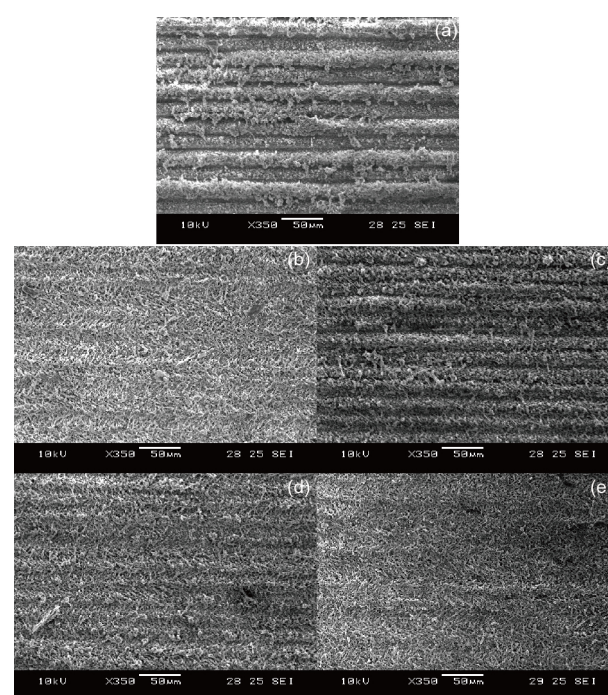
As shown in Figure 6, grooves were observed on the surface, which was relatively rougher at the lower scanning speeds. The groove depths at scanning speed of 1 and 2 mm/s are 24.9 and 11.3 μm respectively. It was observed that the groove structure became shallower and smoother by increasing the scanning speed. At 3 mm/s the groove depth decreased to 5.4 μm and the groove ridges became unclearly defined. Furthermore, it was found that there was little variation of the surface structure with the scanning speeds more than 4 mm/s. Figures 6(d) and (e) showed surface structure at 4 and 12 mm/s with no significant difference between them.



**Figure 4** (Color online) Variation of WCA of laser treated sample over time. Laser treated sample at the fluence of (1) 193.9 J/cm<sup>2</sup>, (2) 169.5 J/cm<sup>2</sup>, (3) 130.2 J/cm<sup>2</sup>, (4) 86.5 J/cm<sup>2</sup>, (5) 48.4 J/cm<sup>2</sup> and (6) 23.1 J/cm<sup>2</sup> [19].

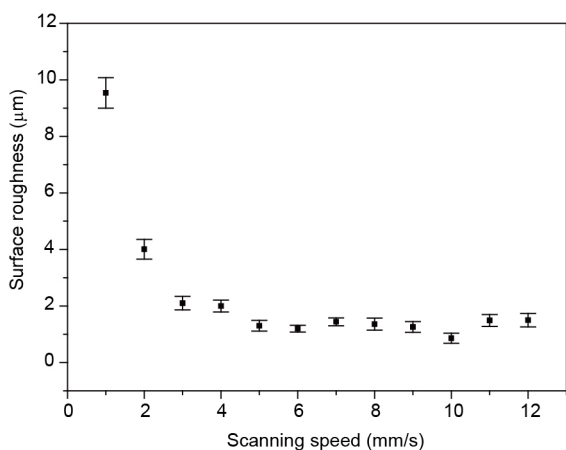


**Figure 5** (Color online) Effect of scanning speed on the surface water contact angle.

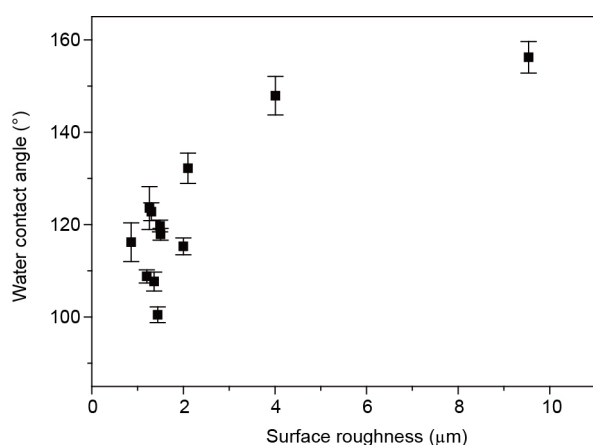


**Figure 6** SEM images of surface structure at different scanning speed. (a) 1 mm/s; (b) 2 mm/s; (c) 3 mm/s; (d) 4 mm/s; (e) 12 mm/s.

structure at 4 and 12 mm/s with no significant difference between them. The surface roughness at different scanning speed is shown in Figure 7. At the lower scanning speeds the surface is generally rough. For example, the surface roughness (Ra) is 9.54 and 4.01 μm at the scanning speed of 1 and 2 mm/s respectively. The variation of surface roughness became insignificant when the scanning speed is above 4 mm/s. Pristine surface roughness (Ra) is measured to be around 7.98 nm. Figure 8 showed the WCA as a function of the surface roughness. It is seen that the WCA increased with an increase in the surface roughness, which can be explained by the Cassie-Baxter's model [22] that the liquid droplet does not completely wet the roughened substrate. When a surface



**Figure 7** Effect of scanning speed on surface roughness. The pristine surface roughness is around 7.98 nm, which is indicated by star in the figure.



**Figure 8** Effect of surface roughness on WCA. The star in the figure presents the WCA of pristine sample.

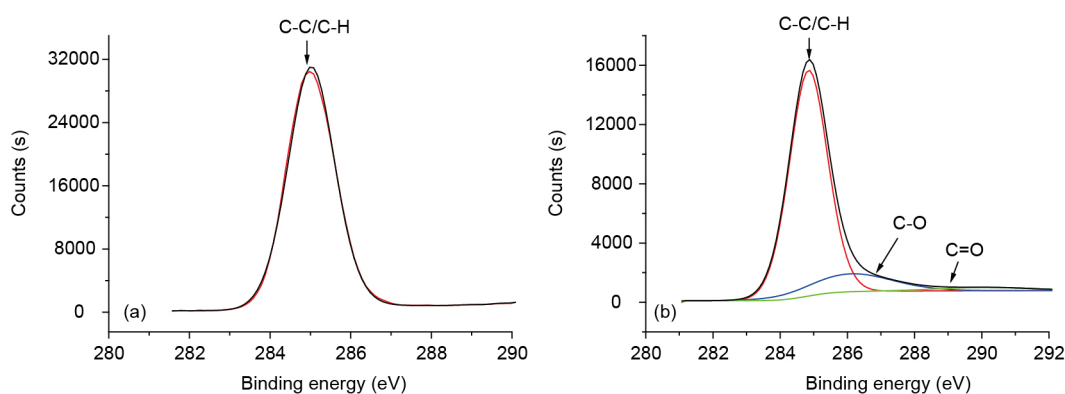
is rough enough (e.g.  $R_a$  larger than 1.2  $\mu\text{m}$ ), air can be entrapped between the liquid and the solid. The interface becomes composite and the contact angle increases with roughness even if the surface chemistry is intrinsically hydrophilic.

It has been reported that the polar (such as C—O, C=O, and O—C=O bonds) and non-polar (such as C—C or C—H

bonds) groups formed on the surface are responsible for the wettability changes [3]. To better understand this phenomenon, chemical bonds formed on the surface were identified by using an X-ray photoelectron spectroscopy (XPS). The main C—C/C—H bond peak is around 285 eV, while the peak of C—O and C=O bonds are around 286 and 289 eV respectively. Figure 9 showed the measured XPS spectra of a pristine surface and a superhydrophobic surface. The detailed bond information was shown in Table 1.

As depicted in Figure 9 and Table 1, the oxygen content (polar group) increased after laser treatment. The total polar groups (at. %) varied with the beam scanning speed, i.e. the beam-material interaction time. At the speed of 1 mm/s, the sum of the polar groups is 17.31 (at. %) and the WCA reached 156.2°, indicating a superhydrophobic condition. The corresponding surface roughness was at a high value of 9.54  $\mu\text{m}$ . The rougher surface textures enabled more air trap between the liquid and the surface, which contributed to the superhydrophobic condition. This may imply that the effect of the polar groups on surface WCA is not always the dominating factor for the surface wettability. For a rough surface, the surface roughness or the surface topography structure played a more significant role in the changes of the surface WCA.

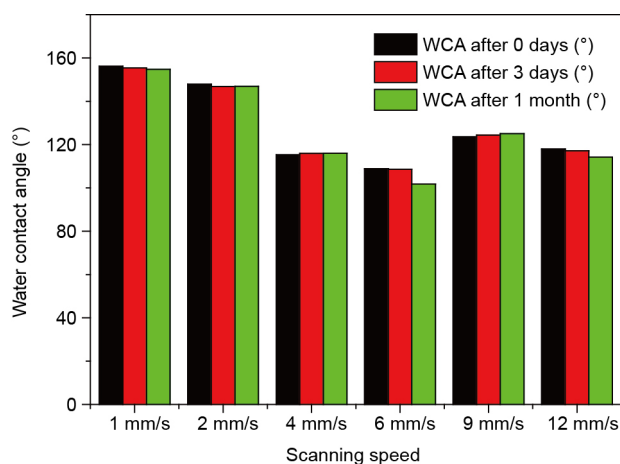
As stated in the hydrophilic modification section (subsect. 3.1), the WCA of a hydrophilic surface tends to restore its original untreated value over time in open air environment after laser treatment. The WCA recovery may be due to reaction between the treated surface (with broken bonds) and air. The WCA recovery of hydrophobic surfaces was also investigated. Figure 10 presents the water contact angle of samples measured at different time after laser treatment, namely immediately after laser treatment (0 days), 3 days and one month after laser treatment. It is seen that the hydrophobic property of the sample surface created by the laser treatment was rather stable, with no or negligible changes over time. This is quite different with hydrophilic surfaces. This may be because a hydrophobic surface with surface water contact angle above 90° has low surface energy; thus there will be no or little reaction between the surface and air over time.



**Figure 9** (Color online) XPS spectra of pristine PS surface (a) and laser treated PS surface (b) at a scanning speed of 1 mm/s.

**Table 1** Polar and non-polar groups of pristine PS and PS surface treated at different scanning speed

Scanning speed (mm/s)	Non-polar groups C—C/C—H (at. %)	Polar group C—O (at. %)	Polar group C=O (at. %)	Sum of polar groups (at. %)	Water contact angle (°)
0	100	—	—	—	88.2
1	82.69	14.23	3.08	17.31	156.2
2	76.44	16.98	6.58	23.56	147.9
6	67.44	28.42	4.14	32.56	108.8
9	73.32	23.91	2.77	26.68	123.6

**Figure 10** (Color online) Variation of WCA of laser treated sample over time at different scanning speed.

## 4 Conclusion

The PS sample was successfully modified to either highly hydrophilic or superhydrophobic with fs laser irradiation. With properly spaced micro-pits created on the surface, the PS sample became more hydrophilic due to the easier penetration of water droplets into the micro-pits. The surface wettability increased with the depth, size and density of the micro-pits. This is consistent with Wenzel's model. While in order to create a superhydrophobic surface, micro-scale grooves were created on the sample surface. The surface roughness was as high as  $9.54\ \mu\text{m}$  in Ra after laser treatment. The air bubbles may have been trapped in between the sample surface and water droplets, thus the surface become more hydrophobic and even superhydrophobic (reached  $156.2^\circ$ ). This is consistent with Cassie-Baxter's model. The variation of surface WCA over time was investigated. WCA recovery was found on hydrophilic surfaces while the surface wettability of hydrophobic surfaces seems stable after laser treatment. For the laser-treated surface with low roughness, the polar (such as C—O, C=O, and O—C=O bonds) and non-polar (such as C—C or C—H bonds) groups were found to be responsible for the wettability changes. While for a rough surface, the surface roughness or the surface topography structure played

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- B. Wang, X. Wang, H. Zheng, and Y. Lam, *Nanomaterials* **5**, 1442 (2015).
- Z. K. Wang, H. Y. Zheng, C. P. Lim, and Y. C. Lam, *Appl. Phys. Lett.* **95**, 111110 (2009).
- J. Lai, B. Sunderland, J. Xue, S. Yan, W. Zhao, M. Folkard, B. D. Michael, and Y. Wang, *Appl. Surface Sci.* **252**, 3375 (2006).
- T. O. Yoon, H. J. Shin, S. C. Jeoung, and Y. I. Park, *Opt. Express* **16**, 12715 (2008).
- C. Y. Lee, B. S. Kim, H. J. Choi, and J. S. Lee, *J. Korean Phys. Soc.* **63**, 1399 (2013).
- H. J. Ramos, J. L. C. Monasterial, and G. Q. Blantocas, *Nucl. Instrum. Methods Phys. Res. Sect. B-Beam Interact. Mater. Atoms* **242**, 41 (2006).
- S. J. Hwang, M. C. Tseng, J. R. Shu, and H. Her Yu, *Surface Coatings Tech.* **202**, 3669 (2008).
- T. Demina, D. Zaytseva-Zotova, M. Yablokov, A. Gilman, T. Akopova, E. Markvicheva, and A. Zelenetskii, *Surface Coatings Tech.* **207**, 508 (2012).
- Y. Nishi, H. Izumi, J. Kawano, K. Oguri, Y. Kawaguchi, M. Ogata, A. Tonegawa, K. Takayama, T. Kawai, and M. Ochi, *J. Mater. Sci.* **32**, 3637 (1997).
- Y. Liu, X. Yin, J. Zhang, Y. Wang, Z. Han, and L. Ren, *Appl. Surface Sci.* **280**, 845 (2013).
- J. H. Lee, H. G. Kim, G. S. Khang, H. B. Lee, and M. S. Jhon, *J. Colloid Interface Sci.* **151**, 563 (1992).
- A. Riveiro, R. Soto, R. Comesaña, M. Boutinguiza, J. del Val, F. Quintero, F. Lusquiños, and J. Pou, *Appl. Surface Sci.* **258**, 9437 (2012).
- L. He, J. Chen, D. F. Farson, J. J. Lannutti, and S. I. Rokhlin, *Appl. Surface Sci.* **257**, 3547 (2011).
- V. Oliveira, B. Nunes, and R. Vilar, *Nucl. Instrum. Methods Phys. Res. Sect. B-Beam Interact. Mater. Atoms* **268**, 1626 (2010).
- H. Pazokian, A. Selimis, J. Barzin, S. Jelvani, M. Mollabashi, C. Fotakis, and E. Stratakis, *J. Micromech. Microeng.* **22**, 035001 (2012).
- A. Ramazani S. A., S. A. Mousavi, E. Seyedjafari, R. Poursalehi, S. Sareh, A. A. Poorfatollah, and A. N. Shamkhali, *Mater. Sci. Eng. C* **29**, 1491 (2009).
- F. Spano, A. Castellano, A. Massaro, D. Fragouli, R. Cingolani, and A. Athanassiou, *J. Nanosci. Nanotech.* **12**, 4820 (2012).
- S. M. Eaton, C. De Marco, R. Martinez-Vazquez, R. Ramponi, S. Turri, G. Cerullo, and R. Osellame, *J. Biophotonics* **5**, 687 (2012).
- B. Wang, *J. Laser Micro/Nanoeng.* **11**, 253 (2016).
- R. N. Wenzel, *J. Phys. Colloid Chem.* **53**, 1466 (1949).
- C. O'Connell, R. Sherlock, M. D. Ball, B. Aszalós-Kiss, U. Prendergast, and T. J. Glynn, *Appl. Surface Sci.* **255**, 4405 (2009).
- A. B. D. Cassie, and S. Baxter, *Trans. Faraday Soc.* **40**, 546 (1944).