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Fabrication of microholes array on titanium foil by a femtosecond laser and a surface's wettability switching

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In this study, an effective method is proposed for controlling a titanium foil surface's wettability. A microholes array series is fabricated on the surface of titanium foil by a femtosecond laser under different laser energy and pulse number. The changes of the titanium surface's morphology are characterized. When placed in a darkroom with high-temperature treatment and immersed in alcohol under UV irradiation, respectively, the femtosecond laser treated surfaces display switchable wettability. It is demonstrated that the changing between Ti—OH and Ti—O prompts the transformation between superhydrophilic and superhydrophobic. Compared with existing reports, the switchable wetting cycle is shortened to 1.5 h. The functional surfaces with switchable wettability have potential applications in oil–water separation and water mist collection.

Keywords: femtosecond laser; titanium foil; microholes array; switchable wettability.

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1. Introduction

In nature, there are many creatures whose surfaces have strong repelling ability to water droplets. For instance, water droplets can roll freely over the lotus leaf, and the water spider can walk on water. Inspired by the special waterproof function of these creatures, a series of significant efforts have been devoted to research on superhydrophobic surfaces[1]. At present, a superhydrophobic functional surface has been widely used in our daily life[2,3].

Due to its high specific strength, low density, excellent corrosion resistance, and good performance in high-temperature environments, titanium (Ti) is widely used in the fields of military, aerospace, shipbuilding, and so on[4]. Due to its unique photocatalytic performance, Ti oxide (TiO_2) could give the original surface switchable wettability, which has aroused extensive interests[5]. Yong and his colleagues used a femtosecond (fs) laser to process micro/nano conical structures on the Ti surface, which could realize switchable wettability under UV irradiation for 60 min and storage in the dark for 48 h[6]. Zhou *et al.* reported a kind of three-level cobblestone-like anatase TiO_2 microcones array, which was fabricated on Ti sheets by fs laser-induced self-assembly. The TiO_2 surfaces displayed dual-responsive water/oil reversible wetting with a conversion cycle of 2.5 h[7]. Yong and co-workers fabricated a microcones array on a zinc sheet by using a fs laser. The ZnO surfaces showed switchable wettability with a conversion cycle of one week[8]. Yong *et al.* processed the micro–nano structures on material surfaces by a fs laser. Combined with ethanol auxiliary, the processed surface realized the switchable wettability of underwater gas[9]. However, the methods mentioned above still have some limitations, such as low conversion efficiency and working only on the Ti surface, which restricts the application of surfaces with switchable wettability.

The fs laser is a new processing method for micro/nano fabrication, which has the characteristics of ultra-short pulse width, high pulse peak power, and low thermal effect. Based on the above advantages, the fs laser could fabricate almost all materials including metals and nonmetals[10–16].

In order to solve the problems mentioned above, an experimental study on fs laser ablation of Ti foil surface and its wettability switching is carried out. A microholes array series is fabricated on Ti foil by a fs laser under different laser energy and pulse number. Also, the changes of the Ti surface's morphology are characterized. The fs laser treated surface's wettability is transformed by placing it in a darkroom with high-temperature treatment and immersing it in alcohol under UV irradiation, respectively. In addition, the mechanism of transformation between superhydrophilic and superhydrophobic is explained.

2. Experiment and Material

The experimental fs laser fabrication system is shown in Fig. 1, which is mainly composed of a fs laser source, an optical

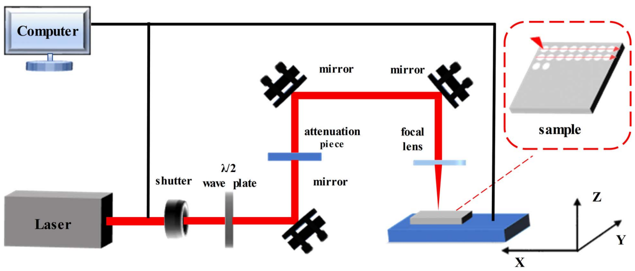

Fig. 1. Fs laser micro/nano fabrication system.

transmission system, a three-dimensional motion platform, and a motion control system. The laser beam (120 fs pulse width) with a repetition rate of 1 kHz, a maximum output power of 5 W, and a central wavelength of 800 nm from a regenerative amplified Ti:sapphire fs laser system (Spectra Physics, USA) was used. In the optical transmission system, a shutter was used to control the on–off time of the optical path, a tunable attenuator was used to adjust the fs laser processing energy, and a lens with 50 mm focal length was used to focus the laser beam. The three-dimensional precision motion platform was used to control the processing motion.

Ti foil (20 mm × 20 mm) with purity of 99.9% and thickness of 30 μm was used in our experiments. Before and after laser processing, the Ti foil was cleaned with acetone, alcohol, and distilled water, respectively, and then dried for 10 min. A laser confocal microscope (Carl Zeiss, Germany) and a scanning electron microscope (SEM, JEOL Ltd., Japan) were employed to analyze the microstructures of the samples. The digital display heating platform (JF-956S) was employed for heating at a temperature of 200°C when the samples were placed on the heating platform and covered with an aluminum plate for the darkroom high-temperature treatment. The UV light irradiation was carried out with a UV lamp with a wavelength of 365 nm and power of 36 W. The samples were immersed in a container containing ethanol and were 5 cm away from the UV lamp. An angular contact (Biolin Scientific, Finland) measuring instrument was used to characterize the wettability of the surface with 12 μL water droplets.

3. Results and Discussion

Figure 2 shows the SEM images of the microholes array on the Ti foil surface fabricated by the fs laser with laser energy of 50 mW and pulse number of 100. Due to the ultra-high peak power density and the precise movement control of three-dimensional motion platform, the microholes array could be accurately fabricated on the Ti foil surface. After fs laser scanning, the laser treated area is cooled and then solidified around the hole to form a ring of the micro–nano recast layer, as presented in Figs. 2(b) and 2(c).

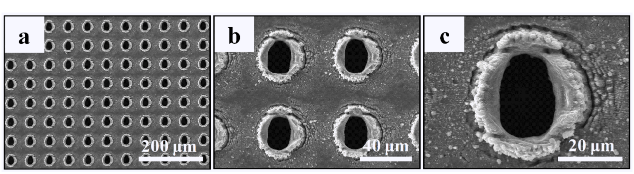

Fig. 2. SEM images of fabricated sample with different magnification: (a) 200 times; (b) 800 times; (c) 2000 times.

Figure 3 depicts the SEM images of samples processed by the fs laser under different energy and pulse number. As displayed in Fig. 3, the laser treated microholes have different sizes under different laser processing parameters. According to Figs. 3(b) and 3(c), when the pulse number is the same, the microhole's diameter increases with the increase of the laser processing energy. When the laser processing energy remains unchanged, the microhole's diameter increases with the increase of the pulse number, as exhibited in Figs. 3(c) and 3(d).

For further exploring the relation between fs laser processing parameters and the microhole's diameter, the effect of laser energy and pulse number on the microhole's diameter was analyzed. Figure 4 shows the laser energy and pulse number dependence of the microhole's diameter generated on Ti samples. It is found that the laser treated microhole's diameter increases with the increase of pulse energy under the same pulse number. Similarly, when the pulse energy remains unchanged, the laser treated microhole's diameter also increases with the increase of the pulse number. As the pulse number is relatively small, the microhole's diameter obviously increases with the pulse number increasing. When the pulse number increases to a certain value, the microhole's diameter is basically unchanged. Therefore, the size of the microholes on the Ti foil could be controlled by adjusting the laser energy and the pulse number, which could regulate the wettability of the surface[17,18].

For the wettability switching experiments, the microholes array with a diameter of 28 μm and a spacing of 60 μm was employed. Before laser fabrication, the measured water contact angle (WCA) of the Ti foil surface was about 35.3°, while the

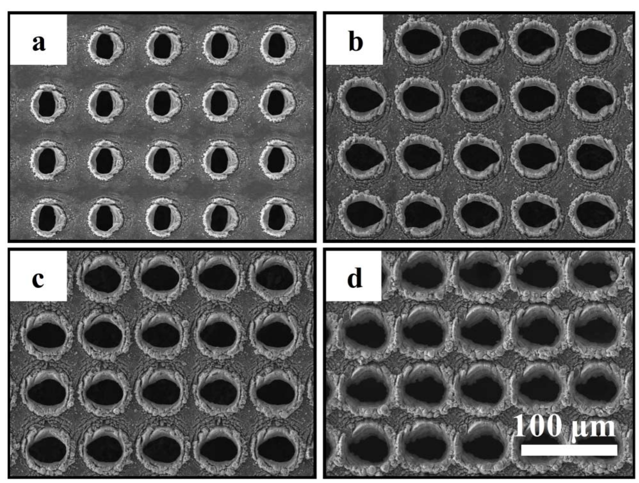

Fig. 3. SEM images of fabricated samples by different fs laser energy and pulse number: (a) 50 mW, 100; (b) 100 mW, 150; (c) 220 mW, 150; (d) 220 mW, 200.

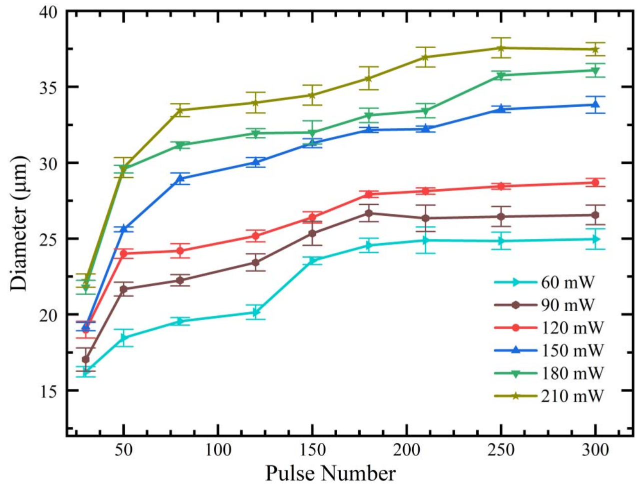

Fig. 4. Fs laser energy and pulse number dependence of microhole's diameter generated on Ti samples.

laser treated sample surfaces were superhydrophilic. This was due to the fact that the edge of the laser treated microholes array was covered by the micro–nano recast layer, which was helpful for the sample surfaces to realize the superhydrophilic properties. The fs laser treated surfaces displayed switchable wettability in air by placing them in a darkroom with high-temperature treatment and immersing them in alcohol under UV irradiation, respectively, as shown in Fig. 5(a). After being heated in a darkroom for 20 min, the fs laser fabricated superhydrophilic sample changed to hydrophobic in air with a WCA of about 132°. As the heating time increased to 30 min, the WCA increased to 156°, as shown in Fig. 5(b). Oppositely, after UV irradiation in alcohol for 30 min, the superhydrophobic sample becomes hydrophilic in air with a WCA of about 80°. As the UV irradiation time increased to 1 h, the WCA decreases to nearly 0°. By this method, the wetting transformational cycle of the laser treated Ti foil sample could be realized. The switchable wettability between superhydrophobicity and superhydrophilicity was repeatable, which was confirmed by cycle tests, as shown in Fig. 5(c).

In order to explore the mechanism of switchable wettability, the original and fs laser treated surfaces were analyzed by energy-dispersive X-ray spectroscopy (EDXS). As manifested in Fig. 6, the original material surface was primarily composed of Ti (atomic fraction of 100%). After fs laser ablation, the atomic fraction of oxygen increased to 38.7%, while the atomic fraction of Ti decreased. It indicates that the Ti surface was oxidized by the fs laser, which covered the surface with rough TiO_2.

TiO_2 is a well-known photo-responsive semiconducting oxide material. The underlying mechanism of switching wettability is closely bound up with the transformation of Ti–OH and Ti–O, as explained in Fig. 7. According to the findings of previous studies[19–21], it could be summarized that the oxygen vacancies would be formed on the Ti surface by photoexcitation. Also, the H_2O coming from the surrounding environment could make competition with O_2 for dissociation and sorption. After

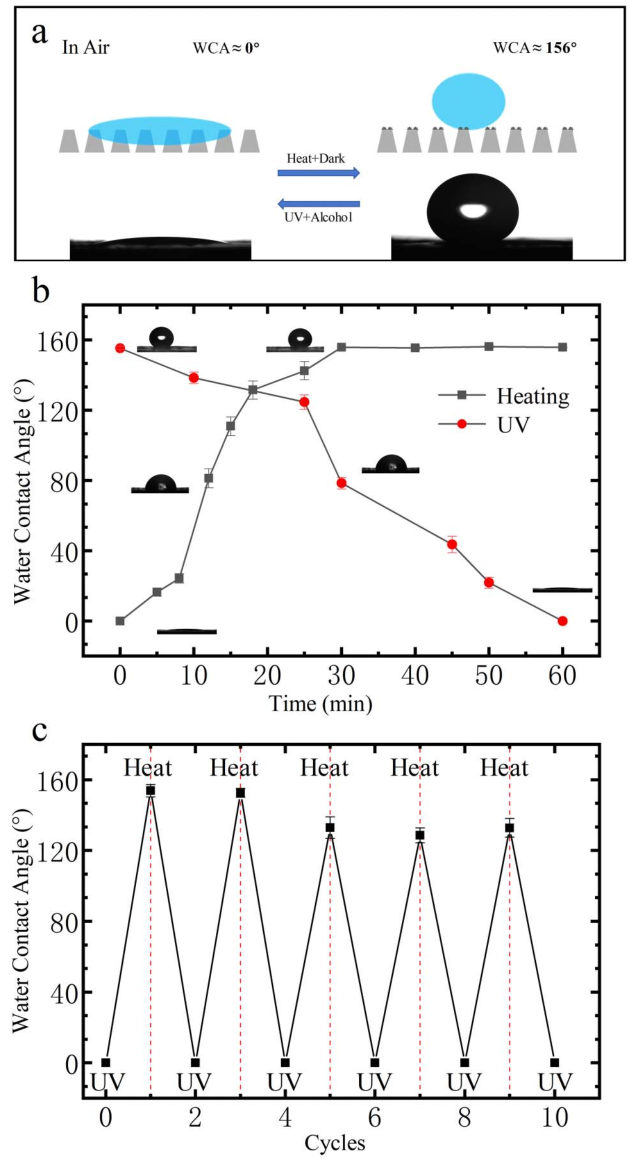

Fig. 5. (a) Schematic diagrams and digital images of the laser treated Ti surface's wettability switching; (b) the WCA of the laser-processed sample under dark heating treatment and UV irradiation for different time; (c) the repeatability of wettability switching.

laser fabrication, plenty of micro-structures were generated on the sample surface, which could enhance the wettability. Also, there were a lot of hydrophilic hydroxyl groups (–OH) on the surface.

Therefore, the laser treated surface displayed steady superhydrophilicity in air. However, during the darkroom high-temperature treatment, the chemical bond Ti–OH of the laser treated surface could be readily displaced by Ti–O. The –OH groups would be quickly displaced by the O_2 coming from the surrounding environment. It would form stable O_2 sorption on the high-temperature treatment surface, which could make the sample remain steady at superhydrophobicity. By immersing in alcohol under UV irradiation for 1 h, instable oxygen

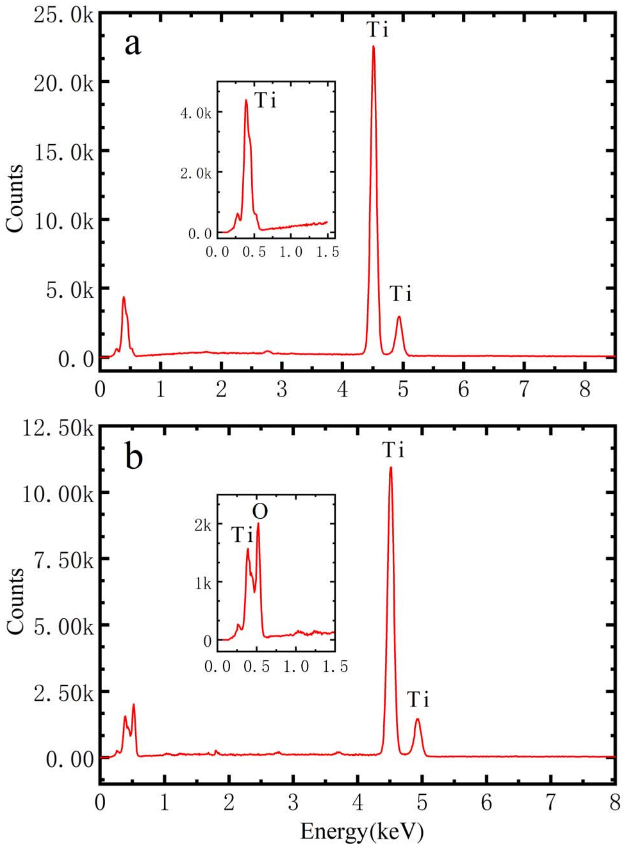

Fig. 6. (a) EDXS results of the Ti sample and (b) that of the Ti surface after fs laser processing.

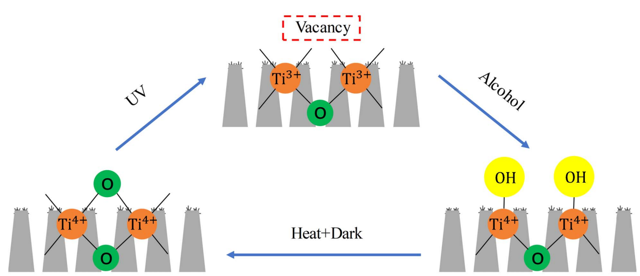

Fig. 7. Mechanism of Ti surface's wettability switching.

vacancies were formed on the fs laser fabricated Ti surface, which had a powerful tendency to dissociate and adsorb −OH. As the alcohol could provide enough −OH, it could greatly reduce the reaction time to promote efficiency. Due to the high surface energy offered by the chemical bond Ti−OH, the superhydrophilicity of the sample was restored. The reversible switching wettability surface proposed here has a probability application value in the aspect of water mist collection and light responsive devices[22].

4. Conclusion

In summary, we report an effective method for the fabrication of a microholes array on the Ti foil surface by a fs laser with switchable wettability. By adjusting the laser energy and the pulse number, the size of the microholes array could be controlled. The fs laser treated surfaces display switchable wettability after being placed in a darkroom with high-temperature treatment and immersed in alcohol under UV irradiation, respectively. Compared with other methods needing several hours or even weeks of conversion period, this method efficiently and rapidly achieves switchable wettability in air by placement in a darkroom with high-temperature treatment (0.5 h) and immersion in alcohol under UV irradiation (1 h). The switchable wettability surface has a good application prospect for water mist collection and light responsive devices.

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