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Superhydrophobic surfaces for polymers with micro and sub-micro scale structure via Two-Photon Polymerization

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Abstract

Due to surface functionalities such as self-cleaning, anti-fogging, and oil-water separation, superhydrophobic surfaces are attractive in many industrial fields. Contact angles greater than 150° can be achieved by fabricating micro-nanostructures and modifying surface energy. Additive manufacturing allows us to overcome the limitations of traditional manufacturing methods in terms of geometrical complexity. This paper reports an investigation on Two-Photon Polymerization (TPP), focusing on the influence of the surface structure types on the wettability performance. Moreover, the micro-structure and sub-micron surface morphology of eggbeater's structure after TPP were also investigated.

Keywords: Superhydrophobic surface, Two-Photon Polymerization, Polymers, Surface structure

1. Introduction

Superhydrophobic surfaces with self-cleaning functionality, oil-water separation capability, anti-fogging, and anti-fouling properties play crucial roles across various industries such as automobile, aerospace, shipbuilding, and medicine [1]. Contact angle (CA) measurements are commonly employed to assess surface wettability. A contact angle higher than 150° typically indicates a superhydrophobic surface. A superhydrophobic surface is attained by either structuring a surface in a hydrophobic base material or modifying the surface chemistry within a micro-nanostructured surface. Developing a universally applicable method to transform a hydrophilic flat surface into a superhydrophobic surface across various materials poses a significant challenge. While several manufacturing techniques exist for creating structured surfaces - including cutting, abrasive machining, beam-based processes, electrical machining, and chemically assisted manufacturing - most struggle to achieve the complexity and high accuracy required for structured surfaces [2]. The emergence of two-photon polymerization (TPP) for crafting sub-microscale 3D structures has opened new avenues for fabricating highly adaptable functional surfaces [3], circumventing the constraints encountered in traditional manufacturing methods when dealing with intricate shapes. This study delves into TPP on the correlation between diverse surface structured shapes and surface wettability and achieves a shift from a hydrophilic with the plat surface to superhydrophobic surfaces with structure solely through alterations in surface structure.

2. Principle

TPP uses pulsed high-energy femtosecond laser beams in a small area [4]. As shown in Figure 1(a) and (b), the resin in the focus plane solidifies when the photoresin molecules simultaneously absorb the energy of two photons. Due to the significant threshold of two-photon polymerization, the rest of the resin can not absorb photons and solidify itself, which means that TPP has high resolution and spatial selectivity [5]. With the movement of the laser focusing point and the stage, the micro and sub-micro scale surface structures are fabricated by curing layer by layer at the desired location.

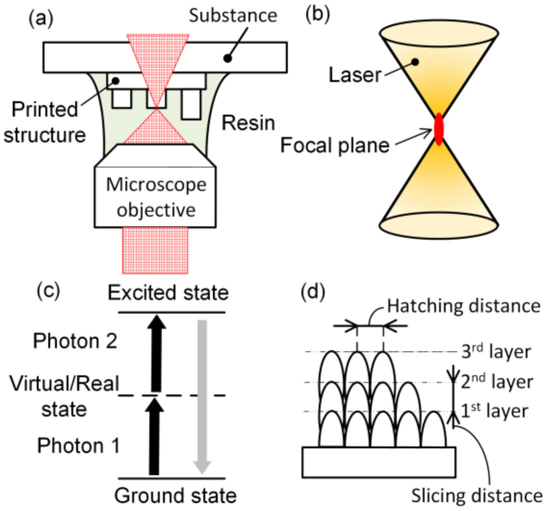

Figure 1. Schematic of two-photon polymerization

3. Experimental details

3.1. Experimental setup

A commercial two-photon polymerization equipment (Nanoscribe Photonic Professional GT) was employed to manufacture structured surfaces, utilizing a maximum power supply of 50 mW. The materials utilized included IP-S Photoresist and glass substrates measuring 25 × 25 × 0.7 mm^3, featuring a one-sided conductive and optically transparent Indium tin oxide (ITO) coating. The surface topography was analyzed using confocal microscopy (Sensofar Neox). Cross-sectional scanning electron microscopy (SEM, FEI QUANTA 450) was employed to visualize the structured surfaces. Surface contact angle was determined by imaging using a Nikon D5300 camera equipped with micro-lens and evaluation through ImageJ software.

3.2. Experimental conditions

The different types of surface structure designs were built as STL, post-processed using DeScribe software, and fabricated using the parameters reported in Table 1. The samples produced through the TPP process underwent a sequential treatment: initially immersed in Propylene glycol monomethyl ether acetate (PGMEA) for 20 minutes, followed by a 5-minute ethanol cleansing stage to eliminate residual resin. Subsequently, the samples were exposed to UV light for 20 minutes to ensure complete curing. Contact angles were obtained as an average of five separate tests, aiming to minimize random errors.

Table 1 The details of experimental parameters

Parameter	Value
Slicing distance	1 µm
Hatching distance	0.5 µm
Laser Power	50 mJ
Scanning speed	100 µm/s

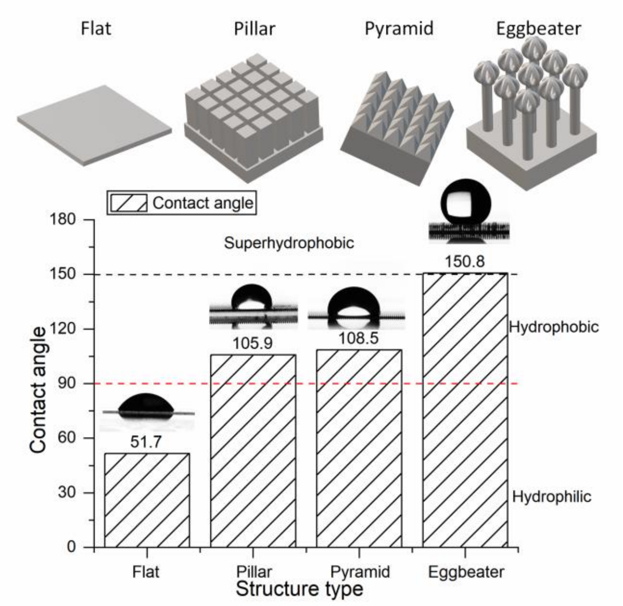

Figure 2. Effect of structure type and contact angle

4. Result and discussion

Figure 2 depicts the relation between various surface structures—Flat, Pillar, Pyramid, and Eggbeater—and their respective contact angles. As per the wettability definition, surfaces exhibiting contact angles exceeding 150° are categorized as superhydrophobic, those below 90° as hydrophilic, and those falling in between as normal hydrophobic surfaces [1]. The contact angle measured for the flat surface registered at 51.7°, characteristic of hydrophilic surfaces. In contrast, both the pillars, measuring 120 µm in height and 45 µm in width, and the pyramid, standing at 50 µm with a width of 50 µm, notably elevate the contact angle. This elevation effectively transforms the wettability from hydrophilic to hydrophobic compared to the flat surface. The base pillar of the eggbeaters exhibits a 20 µm diameter and stands at a height of 120 µm. The top arms comprise 10 µm circles encircling a 40 µm circle. Diverging from pillars and pyramids, the eggbeater-type surface structure achieves a superhydrophobic state. The upper structure of the eggbeater maintains a thin air layer spanning from its base to the top and the droplet is also fixed on the top of the eggbeater structure with hydrophilic surface wettability, demanding greater energy for water to breach this well-defined area [6].

Figure 3 shows the scanning electron microscopic morphologies and surface topography of the eggbeater's structured surfaces. The surface structure has good dimensional accuracy, while the underside of the structure needs to be spliced and fabricated due to the limitations of the lens range. The surface topography and line profile of the top structure after form removal are shown in Figures 3(d) and (e). The structured surface is not completely smooth, but sub-micron structures are created, which is attributed to the slicing distance and hatching distance during the TPP process, as shown in Figure 1(d).

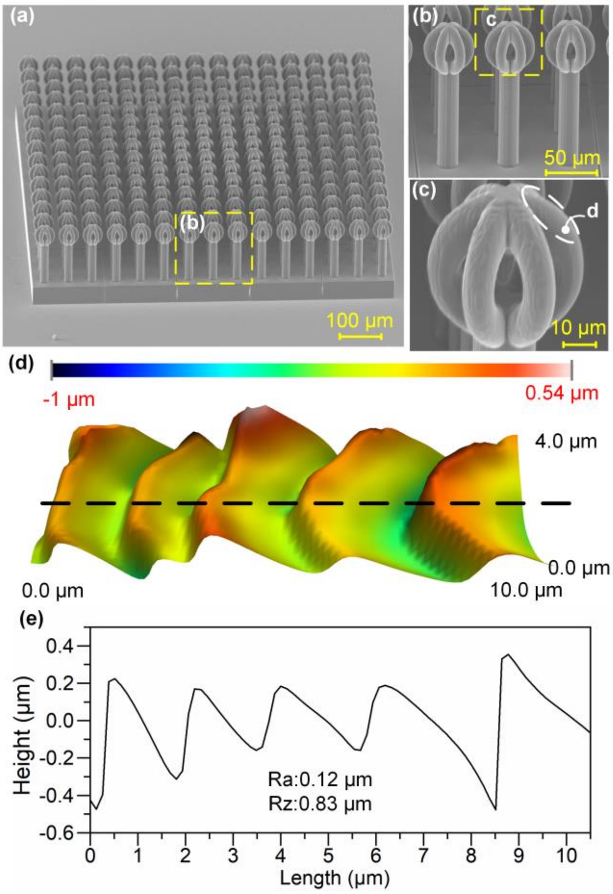

Figure 3. The eggbeater surface structure of SEM Micromorphology (a-c), topography (d), and profile (e).

5. Conclusion

Transforming a hydrophilic flat surface into a superhydrophobic one using typical pillar and pyramid structures presents challenges. Conversely, the eggbeate's structures demonstrate greater ease in achieving superhydrophobicity. The versatility of two-photon polymerization enables enhanced fabrication of intricate three-dimensional structures. Moreover, the sub-micron scale surface morphology is significantly influenced by process parameters, indicating its pivotal role in surface modification.

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