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Multifunctional micro/nano-patterned PTFE near-superamphiphobic surfaces achieved by a femtosecond laser

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ABSTRACT

Near-superamphiphobic polytetrafluoroethylene (PTFE) surfaces exhibiting the robust multifunction capability of self-cleaning, anti-icing, anticorrosion, and mechanical stability were fabricated by femtosecond laser direct writing with no post-processing. The produced surface exhibited contact angles for water and glycol of 157° and 151°, respectively, and water and glycol droplets could easily roll on the laser-treated surface. Furthermore, the produced PTFE surface had an excellent self-cleaning ability demonstrated by depolluting dyed water and glycerol. In addition to these ordinary applications, the laser-treated surface displayed excellent anti-icing ability with good ice delay and icephobic performances. Meanwhile, we find that the near-superamphiphobic surface properties could be maintained following immersion for 2 days in solutions of 98% H_2SO_4, 10 mol/L NaOH, and 40% HF. Further, the obtained near-superamphiphobic surface demonstrated excellent mechanical stability under abrasion and bending tests. Such robust self-cleaning, ice-proof, and anticorrosive near-superamphiphobic surfaces will find diverse applications in industrial fields and in daily life.

1. Introduction

Superamphiphobic surfaces possess a special wettability, comprising both superhydrophobicity and superoleophobicity [1–6]. In nature, materials with the superamphiphobic or near-superamphiphobic property are seldom reported, though surfaces that simultaneously possess hydrophobicity and oleophobicity are actually feasible. Recently, the superb liquid repellency of near-superamphiphobic surfaces has attracted extensive attention and opened up a wide range of applications in the industrial field and daily life including self-cleaning [7,8], anti-sticking [9], anti-icing [10], antifouling [11,12], and energy conversion [13]. Several methods have been developed to process superamphiphobic or near-superamphiphobic surfaces including spraying, electrospinning and chemical vapor deposition [14,15]. More recently, Yuan et al. have reported a spraying technique to achieve nanocomposite coatings with extraordinary superamphiphobic properties on aluminum substrates, which exhibit excellent mechanical and chemical durability and corrosion resistance [16]. Zou et al. have performed an aqueous process for durable superamphiphobic diblock copolymer coatings on fabrics, where they found that fabrics with tunable and robust wettability could be prepared from a copolymer solution at varying concentrations [17]. However, these methods are complicated and time-consuming, requiring a day or more and several steps to prepare the superamphiphobic or near-superamphiphobic surfaces. Moreover, post-production modification is necessary using chemical treatments, which will largely restrict their use in industrial applications. Up to now, using laser technology for making near-superamphiphobic surfaces has scarcely been reported in research literature.

In recent decades, laser direct writing technology, and especially the femtosecond technique, has attracted considerable attention for fabricating high-precision and high-quality microstructures on a variety of materials and for controlling the wettability and optical properties of the samples [18–27]. More recently, using femtosecond laser pulses our group has created a serious of functional surfaces by producing a special hierarchical micro/nanostructure [28–31]. Nevertheless, to our knowledge, high-efficiency processing of a near-superamphiphobic surface with multiple functions using femtosecond laser technology has not been reported in the research literature to date.

In the present study, we create a multifunctional and robust near-superamphiphobic polytetrafluoroethylene (PTFE) surface by producing a hierarchical nano/microstructure with femtosecond laser pulses. The laser-treated near-superamphiphobic surfaces exhibit apparent contact angles larger than 150° and low sliding angles for glycerol and water liquids. Moreover, they possess the combined effects of self-cleaning, anti-icing, anticorrosion and mechanical stability. The self-

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cleaning effect is demonstrated by the inability of dyed water and oil to pollute the laser-treated surface, and whereby each water and oil droplet subsequently removes a significant amount of dust particles from the treated surface. The anti-icing effect is demonstrated by superior ice delay and icephobic performances. The anticorrosion effect is exhibited whereby the property of the near-superamphiphobic surface could be maintained after immersion for 2 days in solutions of 98% H_2SO_4, 10 mol/L NaOH, and 40% HF. Meanwhile, the mechanical stability is verified by long-time test, abrasion test and bending test. We believe that our method for high-efficiency processing of multifunctional near-superamphiphobic PTFE surfaces will find diverse applications in the industrial field and daily life.

2. Material and methods

Polytetrafluoroethylene materials possess many excellent properties, including antiacid/alkali, low- and high-temperature resistance (−180–250 °C), insolubility in organic solvents, strong electrical insulation and resistance to aging. Furthermore, they have been extensively used in the industrial field and in daily life. The square PTFE sample with dimensions of 5 × 5 × 0.1 cm^3 was mounted on a three-dimensional (3D) manual stage, where the schematic of the experiment setup is displayed in Fig. 1(a). A commercial high-repetition femtosecond laser system (PHAROS, LIGHT CONVERSION, Lithuania) was used with a pulse duration of 250 fs, center wavelength of 1030 nm, and repetition of 75 kHz. The laser beam (constant average power of 11 W) was focused on the sample using a two-mirror galvanometric scanner (intelliSCAN III 14, SCANLAB, Germany) with an F-Theta lens (focal length f = 100 mm), and was scanned on the sample surface in the y–z plane. The Gaussian beam produced a focal spot about 20 μm in diameter. The sample was irradiated at a scanning speed of 0.5 m/s, where the interval between adjacent laser scanning lines was 10 μm. All experiments were carried out in air and at room temperature. After laser fabrication, the laser-treated PTFE samples were respectively cleaned using acetone, alcohol, and deionized water in an ultrasonic bath for 10 min. The surface morphologies of the laser-treated samples were analyzed by a MIRA3 LMU scanning electron microscope (SEM, TESCAN, Czech). The 3D profiles of the processed patterns were characterized by an Axio LSM700 laser confocal microscope (LCM, ZEISS, Germany). The contact angles of the water and oil droplets on the surface were measured by a contact-angle system (HARKE, China). All of the presented data are determined using the average value of repeated five measured data [32–34], and the two same SEM images in the manuscript are obtained from the same sample at the same time.

3. Results and discussion

The inset of Fig. 1(a) shows an optical photograph of a laser-treated PTFE sample with dimensions of 5 × 5 × 0.1 cm^3. With the high scanning speed of 0.5 m/s, only 9 min were necessary to fabricate this 5 × 5 cm^2 area. To the best of our knowledge, this is the higher efficiency using laser direct writing technology compared to that in the existing literature [21,27,28,35]. Fig. 1(b) shows the chemical compositions of the original and laser-treated PTFE samples. It can be seen that the element weight of F increases from 61% to 78% while the element weight of C decreases from 39% to 22% after laser treatment. These results indicate that the laser-ablated PTFE surface is fluorated during the formation of the micro/nanostructures. The SEM images at various magnifications of the micro/nanostructures on the PTFE surfaces after femtosecond laser ablation are given in Fig. 1(c)–(e), compared to the untreated surface (Fig. S1). The surface exhibits hierarchical and rough micro/nanopatterns. With the high-resolution SEM image (Fig. 1(e)), it is found that the surface is covered by abundant irregular microcavities and nanoparticles with sizes from tens to hundreds of nanometers. During the interaction between the femtosecond laser and PTFE samples, high-temperature and high-pressure plasma

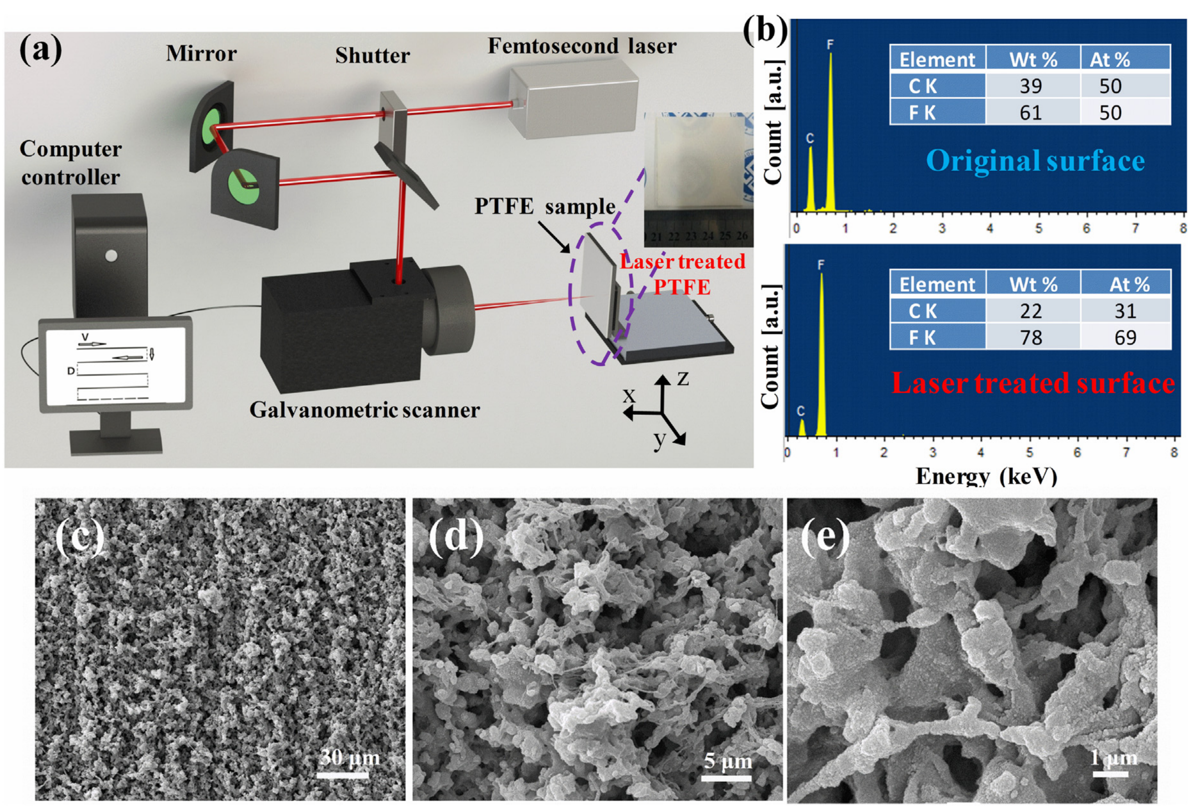

Fig. 1. (a) Schematic of experimental setup. (b) Energy-dispersive X-ray spectroscopy (EDXS) result of the original (upper) and laser-treated (lower) PTFE sample. (c–e) SEM images of the hierarchical micro/nanostructured PTFE surface after femtosecond laser ablation with different magnifications.