A simple and one-step method to form a rough ZnO layer consisting of micro/nanoscale hierarchical structures via direct femtosecond laser ablation of the Zn surface is reported for the first time. The resultant surfaces show switchable wettability between superhydrophobicity and quasi-superhydrophilicity via alternate UV irradiation and dark storage.

The field of artificial intelligence surface was, worldwide, the fastest growing research area in the last decade. Especially, those surfaces which have the unique wetting behaviors have attracted much interest because of their potential fundamental and industrial applications. The most advanced techniques are used to achieve those surface properties which can be used for self-cleaning, anti-icing, anti-blocking, drag reduction, anti-bioadhesion, oil/water separation, and water collection. Nature mimicking is always adopted to achieve the same surface properties. For example, the lotus leaf is at the cutting edge of the development of liquid repellent surfaces. The surface of a lotus leaf is composed of abundant micrometer-sized papillae decorated with nanoscale branch-like protrusions. A layer of epicuticular hydrophobic wax crystal is covered on the rough microstructure of the lotus leaf. The coexistence of the rough surface texture and the chemical layer endows the lotus leaf surface with remarkable superhydrophobicity, and each water droplet on that surface has a contact angle (CA) larger than 150°. Accordingly, a solid surface is considered as superhydrophilic if a water droplet spreads on the surface quickly and exhibits a CA lower than 10°. This kind of surfaces also attract much attention for their excellent water-absorption performance, which is usually applied in water collection. In addition, superhydrophilicity plays a key role in the preparation of underwater superoleophobic surfaces.

Both superhydrophobicity and superhydrophilicity result from the ingenious cooperative interactions of multi-scale rough microstructures and either hydrophobic or hydrophilic chemical composition. Combining these two extreme properties on the same surface—that is, a smart surface that can switch its water wettability—would offer great promise in the design and fabrication of intelligent materials for advanced applications.

Femtosecond laser microfabrication has been proven to be an effective method for controlling the wettability by producing various micro/nanoscale hierarchical rough structures on many solid materials, including silicon, metal, polymer, glasses, and ceramics. Combined with a computer controlled stage, complex two-dimensional (2D) patterns and three-dimensional (3D) microstructures can be precisely realized. Those surfaces exhibit richly colorful wetting properties. Mazur et al. and Stratakis et al., respectively, obtained periodic microscale conical spike forests decorated with nanoscale protrusions through femtosecond laser irradiation of a silicon surface under a reactive gas (SF$_6$) atmosphere. This kind of microstructures is popularly known as “black silicon”. After coating them with a low surface energy monolayer, the resultant surfaces exhibit stable superhydrophobicity and ultralow water adhesion. The high water-repellence property is very close to that of natural lotus leaves. However, the SF$_6$ gas makes the experiment equipment more complex and the fabrication process more cumbersome. In our previous work, we fabricated various microstructures via femtosecond laser scanning processing in an air environment. Superhydrophobicity was easily achieved on silicon and polydimethylsiloxane (PDMS) surfaces. By designing special patterns, unique wettabilities including controllable water adhesion, anisotropic sliding, anisotropic wetting, and directional adhesion were realized. Although superhydrophobic surfaces can be prepared via femtosecond laser ablation, those surfaces show just a single wetting state once a rough microstructure is formed. To the best of our knowledge, the reports about femtosecond laser induced smart surfaces with switchable wetting are still limited until now.

Here, we report a switchable superhydrophobicity on femtosecond laser ablated zinc (Zn) surfaces. Femtosecond laser
Ablation not only forms a micro/nanoscale hierarchical rough structure but also oxidizes the Zn materials, resulting in a rough ZnO layer covering on top of the substrate. The transition from superhydrophobicity to quasi-superhydrophilicity on this laser-induced surface can be reversibly switched by alternate ultraviolet (UV) irradiation and dark storage. The relationships between the CAs and average distances (ADs) of laser pulse ablated points are systematically investigated for both UV irradiated and dark storage surfaces.

The Zn sheets with a thickness of 0.2 mm and purity of 99.9% were pre-polished using a PG-1A metallographic sample polishing machine (Shanghai Metallographic, China). The samples were fixed on a computer controlled moveable platform. The femtosecond laser beam generated from a regenerative amplified Ti:sapphire laser system (CoHerent, Libra-usp-1K-he-200) was perpendicularly focused on the sample surface using a microscope lens with an NA of 0.45 (Nikon, Japan). The basic parameters namely pulse duration, center wavelength, and repetition values are 50 fs, 800 nm, and 1 kHz, respectively. Samples were ablated at a constant power of 15 mW with different ADs which depend on both the scanning speed and the shift of adjacent laser scanning lines. AD is our main processing parameter and reflects the extent of overlapping of laser pulse ablated area. For the detailed definition of AD, the readers are referred to our previous work.26,30,38

Fig. 1 shows the scanning electron microscopy (SEM) images of the femtosecond laser ablated Zn surface at a scanning speed of 2000 μm s⁻¹ and scanning line shift of 2 μm. The surface shows a typical micro/nanoscale binary structure. Micro-mountain-like papillae with size ≈ 8 μm are periodically distributed on the surface with the square as the array. The period is about 10 μm. Every papilla is surrounded by four holes. There are abundant irregular nanoscale protrusions covering on each papilla. The surface roughness (Sₐ) is about 0.667 μm. The micro/nanoscale hierarchical rough structures are considered to be the result of ablation under laser pulses and the resolidification of the ejected particles.39 The hierarchical rough microstructure is also demonstrated by its 3D and cross-sectional profiles using laser confocal scanning microscopy, as shown in Fig. 2. The change in chemistry before and after femtosecond laser irradiation of the Zn surface was investigated using energy dispersive X-ray spectroscopy (EDXS), as shown in Fig. 3. The atomic proportion of Zn is 100% for the bare flat Zn material, whereas it decreases to 67.56% after femtosecond laser irradiation. The laser ablated sample consists of Zn and a new element O. The atomic proportion of O reaches up to 32.44%. The results indicate that oxidation occurs concurrently during the femtosecond laser ablation of the Zn materials, resulting in a rough ZnO layer covering on the original substrate.

Fig. 4a shows a water droplet on the initial femtosecond laser ablated surface. The droplet is of spherical shape with a CA of 159.5° ± 2°. Superhydrophobicity is exhibited by the as-prepared surface at this moment. When the surface is tilted by an angle of 8°, the droplet can easily roll off, indicating ultralow water adhesion (Fig. 4c). This ultralow adhesive superhydrophobicity is indicative of the Cassie–Baxter wetting state; that is, there is an air cushion trapped between the rough surface microstructure and the water droplet.40,41 That is why we can observe a silver mirror on the laser-induced region after
Reversible switching between superhydrophobicity and quasi-superhydrophilicity on femtosecond laser ablated Zn surface (AD = 2 μm) by alternate UV irradiation and dark storage. (a and b) Images of a water droplet on the as-prepared surface after dark storage (a) and UV irradiation (b), respectively. (c) Water droplet rolling off on an 8° tilted as-prepared surface after dark storage. (d) Time sequence of a water droplet contacting and spreading out on the laser-induced surface after UV irradiation.

Fig. 4

Fig. 5 Relationship between surface wettability and AD on the laser induced surface.

The switchable wettability of the femtosecond laser arises from the formation of a rough ZnO microstructure. ZnO is a well-known photo-responsive semiconducting oxide material. Electron–hole pairs are generated on the ZnO surface when the as-prepared surface is irradiated with UV light.43–47 These holes interact with lattice oxygen to produce unstable oxygen vacancies which tend to absorb atmospheric water to form high-surface-energy hydroxyl radicals. The presence of hydroxyl groups makes the as-prepared surfaces change from hydrophobic to hydrophilic. However, when the as-prepared rough ZnO surfaces are stored in a dark environment, the newly implanted hydroxyl groups are easily replaced by ambient oxygen.43–47 As a result, the samples regain their original hydrophobic property. With the wettability amplification effect of rough surface microstructures, the reversible switching behavior between superhydrophobicity and quasi-superhydrophilicity can even be realized on femtosecond laser ablated Zn surfaces by alternate UV irradiation and dark storage.1–3 This switchable wettability is ascribed to the advantage of femtosecond laser ablating metal materials which not only oxidizes the Zn material but also generates hierarchical rough microstructures on the surface. The former endows the resultant ZnO layer with the switching property between hydrophobicity and hydrophilicity, while the latter strongly amplifies the wettability properties.

Fig. 5 presents the influence of the AD on the surface wettability of the laser induced surface. After dark storage, the CA values decrease from 159.5° ± 2° to 151° ± 4.5° and then to 116° ± 6° as AD increases from 2 μm to 5 μm and then to 16 μm. The as-prepared surfaces show superhydrophobicity when AD is no more than 5 μm. In contrast, the wettability changes from quasi-superhydrophilicity (CA = 14.5° ± 3.5°) to ordinary hydrophilicity (CA = 80.6° ± 5°) with the increase of AD from 2 μm to 16 μm when the laser ablated samples are irradiated by UV light for enough time. The trend reveals that both the hydrophobicity (after dark storage) and hydrophilicity (after UV irradiation) weaken with the increasing AD. The surface microstructure has an amplification effect on the wettability of the solid substrate, which results in hydrophobic materials being more hydrophobic and hydrophilic materials being more hydrophilic.37,28 Because AD refers to the average distance of adjacent laser pulse ablated points, the accumulated laser power per unit area at small AD is more than that at larger AD. Larger femtosecond laser power accumulation always gives rise to a stronger interaction of light and solid materials, endowing the surface with more uneven structures. SEM images show that the microscale structures decrease with increasing AD although all laser ablated samples are covered by a layer of nanoscale protrusions (Fig. 1 and Fig. S3, ESI†). The decreased surface roughness weakens the amplification effect of the rough microstructure as well as the hydrophilicity of the dark stored samples and the hydrophilicity of the UV irradiated samples, respectively (Fig. 5).

In conclusion, smart switchable superhydrophobic surfaces have been developed on a femtosecond laser ablated Zn surface. Both the formation of hierarchical rough microstructure and oxidation occur during the process of femtosecond laser ablating Zn materials, resulting in a rough ZnO layer covering on the substrate. The wettability of the as-prepared surface can
be reversibly switched between superhydrophobicity and quasi-superhydrophilicity by alternate UV irradiation and dark storage. This switchable wettability takes advantage of femtosecond laser ablation, which not only oxidizes the metal but also induces hierarchical rough microstructures.

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Notes and references