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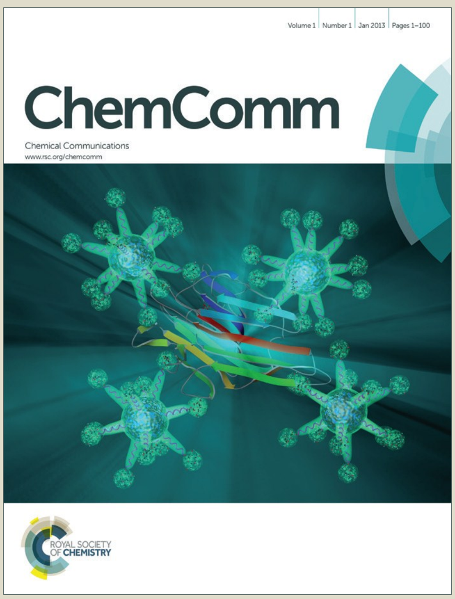

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COMMUNICATION

Femtosecond Laser Induced Hierarchical ZnO Superhydrophobic Surfaces with Switchable Wettability

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

Artificial intelligent surface is the worldwide most growing research 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.[1-3] The most advanced techniques are used to achieve those surface properties which can be used for self-cleaning,[4] anti-icing,[5] anti-blocking,[6] drag reduction,[7] anti-bioadhesion,[8] oil/water separation,[9-11] droplet transfer,[12,13] and water collection.[14] Nature mimicking is always adopted to get those same surface properties.[15-18] For example, lotus leaf is on the cutting edge in developing liquid repellent surfaces.[19,20] Its surface 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 lotus leaf. The coexistence of the rough surface texture and the chemical layer endows lotus leaf surface with remarkable superhydrophobicity, which 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°.[21,22] This kind of surfaces also attracts much attention for their excellent water-absorption performance, which is usually applied in water collection.[23,24] In addition, superhydrophilicity plays a key role on preparing underwater superoleophobic surfaces.[25,26] Both superhydrophobicity and superhydrophilicity result from the ingenious cooperative interactions of multi-scale rough microstructures and either hydrophobic or hydrophilic chemical compositions.[1-3,27,28] Combining these two extreme properties on the same surface; that is, a smart surface 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 to control the wettability by producing various micro/nanoscale hierarchical rough structures on many solid materials, including silicon, metal, polymer, glasses, and ceramics.[29-37] Combined with a computer controlled stage, complex two-dimensional (2D) patterns and three-dimensional (3D) microstructures can be precisely realized.[31-35] Those surfaces perform 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.[36,37] This kind of microstructures is popular as so-called "black silicon". After coating them with low surface energy monolayer, the resultant surfaces show stable superhydrophobicity and ultralow water adhesion. The high water-repellent 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 by a femtosecond laser scanning processing in air environment.[30-35] 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 by femtosecond laser ablation, those reported surfaces show just a single wetting state once rough microstructure is formed. To the best of our knowledge, the report

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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 stored surfaces.

The Zn sheets with thickness of 0.2 mm and purity of 99.9% were pre-polished by 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 NA of 0.45 (Nikon, Japan). The basic parameters including pulse duration, center wavelength, and repetition are 50 fs, 800 nm, and 1 kHz, respectively. Samples were ablated at a constant power of 15 mW with different ADs which are depend on both the scanning speed and the shift of adjacent laser scanning lines. AD is our mainly processing parameter and reflects the extent of overlapping of laser pulses ablated area. The detailed definition of AD can refer to our previous work.[26,30,38]

Figure 1 shows the scanning electron microscope (SEM) images of the femtosecond laser ablated Zn surface at scanning speed of 2000 μm/s and scanning line shift of 2 μm. The surface shows a typical micro/nanoscale binary structure. Micro-mountain-liked papillae with size ≈ 8μm periodically distribute 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 (S_a) is about 0.667 μm. The micro/nanoscale hierarchical rough structures are considered as the result of ablation under laser pulses and the resolidification of ejected particles.[39] The hierarchical rough microstructure is also demonstrated by its 3D and cross-sectional profiles using a laser confocal scanning microscope, as shown in Figure 2. The change in chemistry before and after femtosecond laser irradiating Zn surface was investigated by energy dispersive X-ray spectroscopy (EDXS), as shown in Figure 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 new element of O. The atomic proportion of O reaches up to 32.44%. The results indicate that oxidation happens concurrently during femtosecond laser ablating Zn materials, resulting in a rough ZnO layer covering on the original substrate.

Figure 4a shows a water droplet on the initial femtosecond laser ablated surface. The droplet is in a spherical shape with CA of 159.5° ± 2°. Superhydrophobicity is presented by the as-prepared surface at this moment. When the surface is tilted with an angle of 8°, the droplet can easily roll off, indicating ultralow water adhesion (Figure 4c). This ultralow adhesive superhydrophobicity is indicative of Cassie-Baxter wetting state; that is, there is an air cushion trapped between rough surface microstructure and water droplet.[40,41] That is why we can observe a silver mirror on the laser induced region after immersing the as-prepared sample in water. The mirror-like interface is due to an air layer between the water and as-prepared surface. Interestingly, the wettability of as-prepared surface can switch from superhydrophobicity to quasi-superhydrophilicity by UV light irradiating the sample for 1 day (Figure S1a, ESI). UV light irradiation was carried out with a UV lamp with wavelength of 370 nm and power of 36 W. The distance between the light source and the samples was approximately 7 cm. At present, the CA is as low as 14.5° ± 3.5°, as shown in Figure 4b. When a water droplet is put onto the sample, the droplet will spread out quickly once it contacts the substrate (Figure 4d). The laser induced rough microstructure is fully wetted by water. This indicates that the quasi-superhydrophilicity is at Wenzel wetting state.[41,42] Superhydrophobic state can be re-obtained through storing the sample for 1 week in dark (Figure 4a,b and Figure S1b, ESI). Such a reversible switching between superhydrophobic and quasi-superhydrophilic states on the femtosecond laser induced hierarchical ZnO surface was very well retained after many cycles by the alternate UV irradiation and dark storage (Figure S2, ESI).

The switchable wettability of femtosecond laser arises from the formation of rough ZnO microstructure. ZnO is a well-known photo-responsive semiconducting oxide material. Electro-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 adsorb atmospheric water to form high-surface-energy hydroxyl radicals. The presence of hydroxyl groups makes the as-prepared surface 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 re-obtain its 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 makes the Zn material be oxidized but also generates hierarchical rough microstructures on the surface. The former endows the resultant ZnO layer with switching property between hydrophobicity and hydrophilicity while the latter strongly amplifies those wettability properties.

Figure 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° to151° ± 4.5° and then to116° ± 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 5μm. On the contrary, 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 increasing the AD. Surface microstructure has an amplification effect on

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wettability of solid substrate, which results in hydrophobic materials being more hydrophobic and hydrophilic materials being more hydrophilic.[27,28] Because AD refers the average distance of adjacent laser pulse ablated points, the accumulated laser power per unit area at small AD is more than that at lager 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 AD increasing although all laser ablated samples are covered a layer of nanoscale protrusions (Figure 1 and Figure S3, ESI). The decreased surface roughness weakens the amplification effect of rough microstructure, as well as the hydrophobicity of dark stored samples and the hydrophilicity of UV irradiated samples, respectively (Figure 5).

In conclusion, smart switchable superhydrophobic surfaces are developed on femtosecond laser ablated Zn surface. Both the formation of hierarchical rough microstructure and oxidization 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 reversible 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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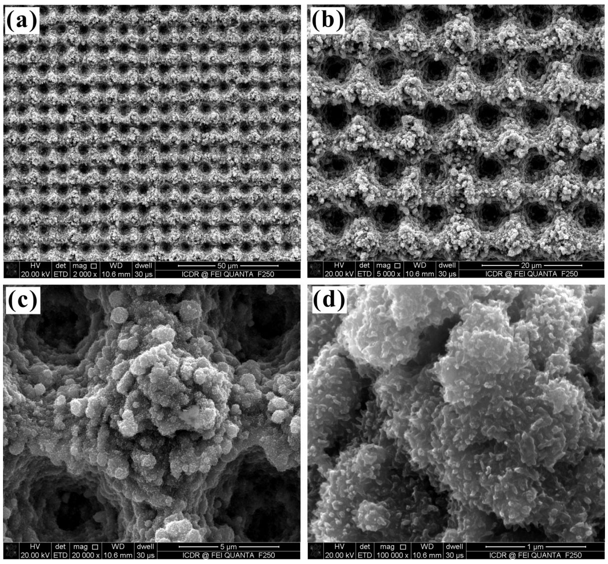

Figure 1. SEM images of Zn surface after femtosecond laser ablation. The surface was irradiated at speed of 2000μm/s and shift of 2μm; that is, AD = 2μm.

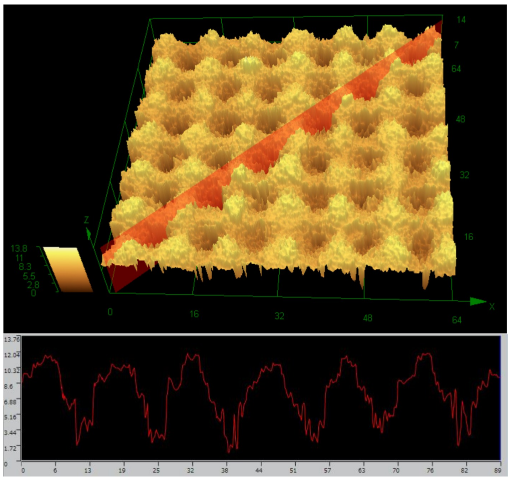

Figure 2. 3D image and cross-sectional profile of the femtosecond laser ablated surface (AD = 2μm).

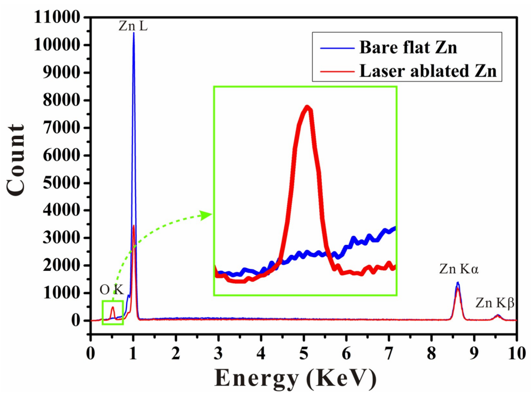

Figure 3. EDXS results of the Zn material before and after femtosecond laser ablation (AD = 2μm).

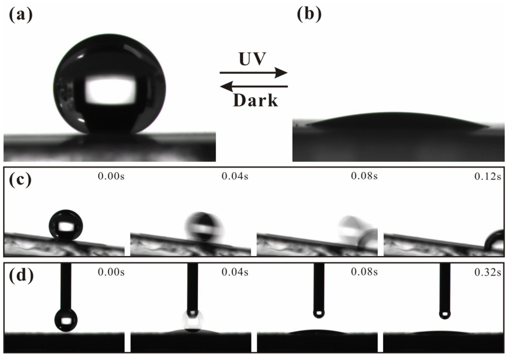

Figure 4. Reversible switching between superhydrophobicity and quasi-superhydrophilicity on femtosecond laser ablated Zn surface (AD = 2μm) by alternate UV irradiation and dark storage. (a,b) Images of a water droplet on the as-prepared surface after dark storage (a) and UV irradiation (b), respectively. (c) Water droplet rolling off on an 8° tiled 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.

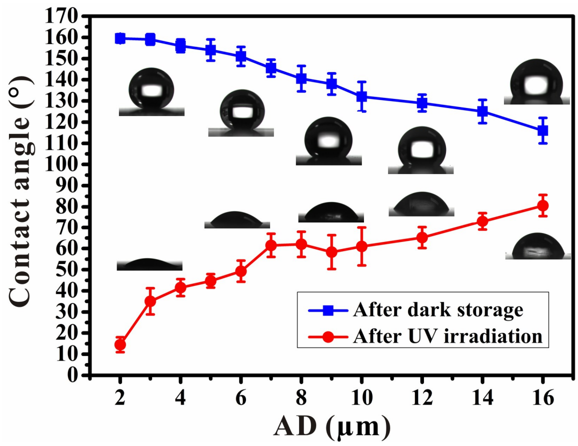

Figure 5. Relationship between surface wettability and AD on the laser induced surface.

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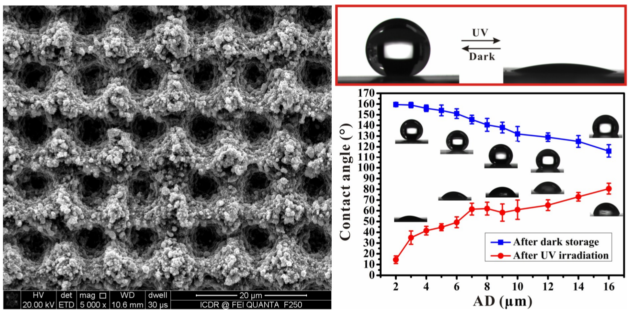

A table of contents entry

Hierarchical rough ZnO layer is directly induced from Zn Substrate by a one-step femtosecond laser ablation and shows switchable wettability.

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