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Laser ablation processing of zinc sheets in hydrogen peroxide solution for preparing hydrophobic microstructured surfaces

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ABSTRACT

Hydrophobic microstructured surfaces were prepared by nanosecond (ns) and femtosecond (fs) laser ablation of zinc sheets in hydrogen peroxide aqueous solution. It was found that ZnO and $Zn(OH)_2$ were generated after ns or fs laser ablation. The ns laser-ablated sample, on which clustered flower-like microstructures composed of nanoneedles occurred, exhibited superhydrophobicity with a water contact angle (WCA) of 158.5° and a water sliding angle (WSA) of 4.3°. In contrast, the fs laser-ablated sample, which was covered with non-directional flaky nanostructures, showed high hydrophobicity with a WCA of 145.7° and a WSA of 12.5°. The one-step method proposed here may be useful for fabricating self-cleaning functional surfaces and devices.

1. Introduction

From the viewpoint of wettability, surfaces of solid materials have generally been classified as hydrophobic (with water contact angles (WCAs) larger than 90°) and hydrophilic (with WCAs lower than 90°) [1]. As special cases of hydrophobic surfaces, superhydrophobic surfaces, which are defined as structured (or non-smooth) surfaces with WCAs of 150° or larger and water sliding angles (WSAs) lower than 5–10° [2], have attracted much more attention for fundamental interest and practical applications [3]. It is well known that the wettability of a surface is governed by its chemical and physical properties [4]. Since the WCA of a man-made or natural flat surface even with the lowest surface energy is not larger than 119°, WCAs of 150–174° displayed for most superhydrophobic surfaces can only be achieved by manipulating surface roughness and/or microstructure [5,6].

Up to now, many preparation methods, such as chemical vapor deposition [7], wet chemistry process [8,9], nanoimprint lithography [10], laser etching [11], have been reported to produce microstructures on material surfaces to obtain superhydrophobicity. In recent years, a pulsed laser ablation (PLA) technique has been successfully developed due to its virtues of relatively low cost, simple procedure and minimum amount of chemical species [12]. However, there is no report on PLA of zinc (Zn) in hydrogen peroxide solution and its effect on wettability of the as-prepared microstructured ZnO-based surfaces. As known to all, ZnO-based materials find numerous applications, particularly in the fields of photocatalysis, chemical sensors, memory resistors, photovoltaics and spintronics owing to their excellent dielectric, ferroelectric, piezoelectric, pyroelectric, photoelectric and ferromagnetic (if they are doped by “magnetic” atoms) properties [5,9]. On other hand, although both nanosecond (ns) and femtosecond (fs) lasers can be adopted in the PLA technique, the resulted structure characteristics and functional features may be much different from each other [11].

In the present work, we demonstrated the formation of microstructures on Zn sheets by one-step ns and fs PLA in hydrogen peroxide solution. The structure characteristics and wetting properties of various laser-ablated Zn sheets were investigated. The effect of laser ablation on wettability of the microstructured surfaces was discussed.

2. Experimental procedure

Zn sheets (Φ8 mm × 0.3 mm, 99.99% purity) were fixed on the bottom of a glass vessel filled with 10 mL of hydrogen peroxide aqueous solution (3 M). The upper surfaces of the Zn sheets were

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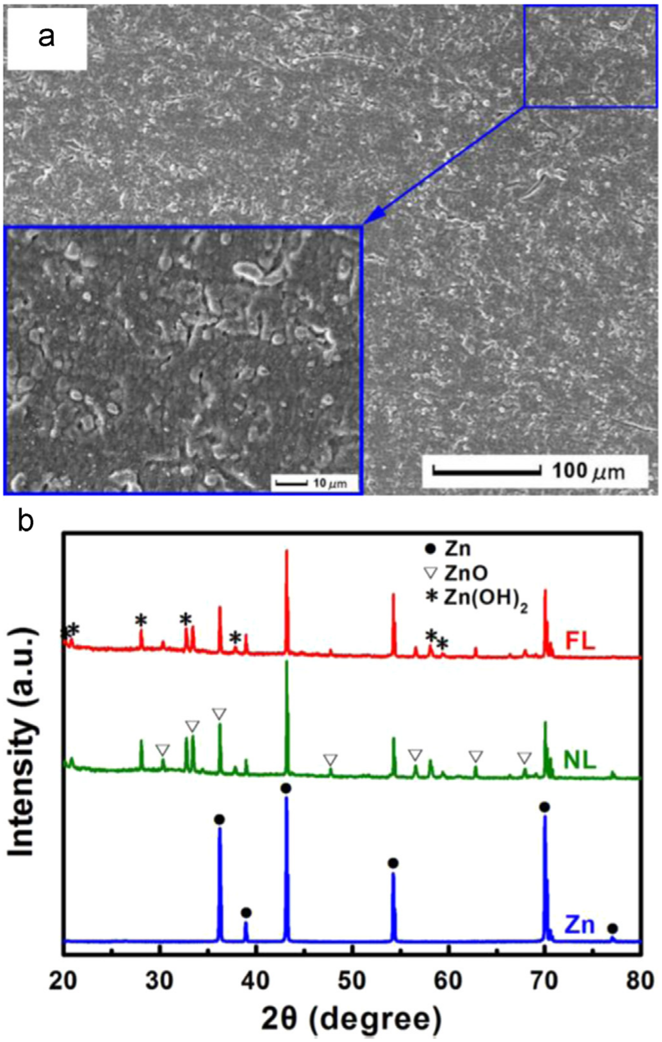

Fig. 1. (a) SEM images of sample Zn. (b) XRD patterns of different samples.

positioned 2 mm below the liquid surface and ablated using a diode pumped Nd:YVO_4 ns pulsed laser system (532 nm) and a regenerative/multi-pass Ti:sapphire fs amplifier system (800 nm), respectively. Both the ns and fs laser beams were focused to a beam diameter of ~3 mm and vertically irradiated on the surfaces of the Zn sheets with a defocus amount of −0.1 mm. The laser fluence was 1 J/cm^2 and the ablation time was 20 s for the both cases. The original Zn sheet, the ns and fs laser-ablated Zn sheets were denoted as Zn, NL and FL, respectively.

Surface morphology was observed using a scanning electron microscope (SEM, JEOL JSM-7001F). An X-ray diffractometer (XRD, Bruker D8 Advance) was adopted to examine crystal phase. Surface root mean square (RMS) roughness was obtained through an atomic force microscope (AFM, Asylum Research MFP-3D-SA). WCA and WSA were tested by a contact angle goniometer (Dataphysics OCA20) using 1 μL of water droplets.

3. Results and discussion

The low-magnification SEM image of sample Zn in Fig. 1(a) shows a relatively flat surface. From the partial enlarged view in Fig. 1(a), only few granulated protrusions at the scale of several micrometers can be observed.

Fig. 1(b) shows the XRD patterns of samples Zn, NL and FL. All the samples exhibit the diffraction peaks that can be indexed to the hexagonal phase of Zn (JCPDS no. 65-3358). Samples NL and FL also display strong peaks that are in good agreement with the standard data of JCPDS nos. 36-1451 and 38-0385, respectively indicating the presence of ZnO hexagonal wurtzite phase and $Zn(OH)_2$ orthorhombic phase. The formation of $Zn(OH)_2$ and ZnO should be attributed to the following reactions between metallic zinc and hydrogen peroxide solution during laser ablation [13].

$$Zn + H_2O_2 \rightarrow Zn(OH)_2(S) \tag{1}$$

$$Zn(OH)_2 \rightarrow ZnO(S) + H_2O \tag{2}$$

Compared with those of sample Zn, the Zn peaks in the XRD patterns of samples NL and FL show marked decrease in intensity, which can be ascribed to the coverage of the generated ZnO and $Zn(OH)_2$ on the sample surfaces [14]. In addition, comparing the intensities of ZnO peaks reveals the random orientation of ZnO crystals in samples NL and FL [15].

The low- and high-magnification SEM images of samples NL and FL are shown in Fig. 2. It is noteworthy that the morphology on the surfaces of both samples are quite different, which may be related to that ns laser can cause stronger heat effect in comparison with fs laser [16]. The ns laser-ablated sample is covered with clustered flower-like microstructures (1–10 μm in diameter) containing ZnO and $Zn(OH)_2$ crystals (Fig. 2(a)). By a detailed observation, the individual flower-like microstructure is found to be composed of nanoneedles with widths of 80–300 nm (Fig. 2(b)). After fs laser ablation, as Fig. 2(c) shows, fragment-like ZnO and $Zn(OH)_2$ crystals occur on the sample surface. From the high-magnification view (Fig. 2(d)), non-directional flaky nanostructures of ~200 nm in thickness are observed. Obviously, both samples are quite fine-grained and therefore contain very developed free surfaces and grain boundaries, which can significantly affect the physical properties of the samples [9,17]. However, owing to the densely clustered arrangement of the microstructures, sample NL seems to possess more free surfaces and grain boundaries than sample FL.

Table 1 lists the measured surface RMS roughnesses of different samples. The surface RMS roughness of sample Zn is 25.5 nm. Due to the formation of surface microstructures, both samples NL and FL exhibit notable increases in surface RMS roughness. The difference in surface roughness of the two samples (95.7 nm vs 71.4 nm) is believed to be resulted from the different arrangements and feature sizes of surface microstructures as mentioned above.

Fig. 3 presents the photographs of water droplets on the surfaces of different samples during WCA and WSA measurements. The measured results are listed in Table 1. Sample Zn is hydrophilic having a WCA of 32.6°. The measured WCA and WSA of sample NL are 158.5° and 4.3°, respectively, indicating superhydrophobicity of the sample surface. Sample FL is highly hydrophobic with a WCA of 145.7° and a WSA of 12.5°.

The effect of laser ablation processing on wettability of the sample surfaces can be understood by considering three aspects as follows. First, the generation of ZnO and $Zn(OH)_2$ crystals originated from laser ablation (as verified by XRD analysis) lowers the surface free energy of the Zn sheets, which is conducive to improving surface hydrophobicity [4]. Second, surface roughness is an important factor to determine wettability of a surface. It is well known that a rougher surface can contain more air to more effectively prevent the expansion of a water droplet on the surface [5]. Consequently, the laser-ablated Zn sheet with a higher value of surface RMS roughness tends to exhibit a larger WCA. Third, although a superhydrophobic surface requires a large surface roughness and a low surface energy [18], a micro/nanoscale hierarchical structure is the root cause of achieving surface superhydrophobicity [11]. It can thus be stated