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Nanosecond laser textured superhydrophobic metallic surfaces and their chemical sensing applications

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ABSTRACT

This work demonstrates superhydrophobic behavior on nanosecond laser patterned copper and brass surfaces. Compared with ultrafast laser systems previously used for such texturing, infrared nanosecond fiber lasers offer a lower cost and more robust system combined with potentially much higher processing rates. The wettability of the textured surfaces develops from hydrophilicity to superhydrophobicity over time when exposed to ambient conditions. The change in the wetting property is attributed to the partial deoxidation of oxides on the surface induced during laser texturing. Textures exhibiting steady state contact angles of up to ~152° with contact angle hysteresis of around 3–4° have been achieved. Interestingly, the superhydrobobic surfaces have the self-cleaning ability and have potential for chemical sensing applications. The principle of these novel chemical sensors is based on the change in contact angle with the concentration of methanol in a solution. To demonstrate the principle of operation of such a sensor, it is found that the contact angle of methanol solution on the superhydrophobic surfaces exponentially decays with increasing concentration. A significant reduction, of 128°, in contact angle on superhydrophobic brass is observed, which is one order of magnitude greater than that for the untreated surface (12°), when percent composition of methanol reaches to 28%.

1. Introduction

Controlling surface wettability has attracted increased research attention due to the wide range of applications ranging from domestic innovations such as self-cleaning glass to high-technology fields like microfluidic control, corrosion resistance, water–oil separation and drag reduction [1–4]. New applications are continuously being discovered, for instance, the use of low wetting surfaces for the realization of microdroplet lasers [5,6]. Recently, the developments in designing and preparing novel surfaces with special wettability have opened opportunities to employ these surfaces for liquid transportation and smart sensing devices [7,8].

Today, superhydrophobic surfaces on glasses, semiconductors, polymers and metals can be generated by various methods, including lithography, plasma treatment, chemical deposition, colloidal assembling, templating, and ultrafast laser surface texturing [9]. Among these options, laser patterning is a promising method due to the potentially high fabrication speeds, low waste and maskless single-step processing [10–13]. This technology is also highly suitable for producing superhydrophobic surfaces with selective area patterning [14,15].

Superhydrophobic metallic surfaces based on laser texturing have been investigated previously [16,17]. However, to date, most of the reported works rely on high-cost, complex ultrafast (femto-/pico-second) lasers [16–23]. For these lasers, the pulse energy is relatively low so high pulse overlapping is required for creating the surface modification and therefore processing rates are slow. For real industrial applications, the ability to create superhydrophobic metallic surfaces using compact, robust and cost–effective alternatives with fast processing times, such as nanosecond fiber lasers, would be highly desirable.

Copper and brass are widely used for electronic components and industrial devices due to their high electrical and thermal conductivity. However, they are easily affected by environmental conditions, such as high humidity leading to corrosion. Recently, it

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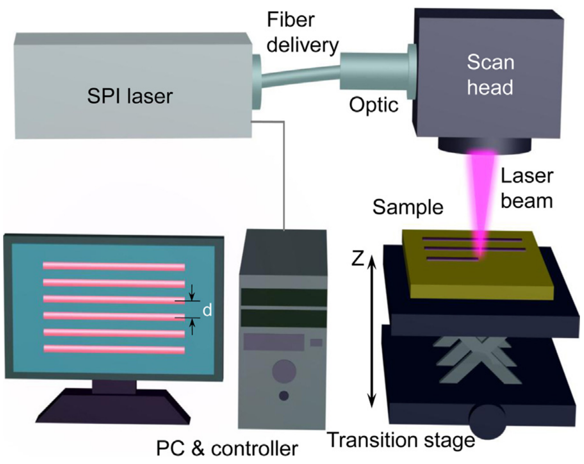

Fig. 1. Schematic of optical setup for fabrication of microgroove structures on copper and brass surfaces.

has been shown these problems can be prevented on these materials by creating a superhydrophobic surface [24].

In this paper, the superhydrophobic behavior of copper and brass surfaces achieved by infrared nanosecond laser surface texturing is presented. The superhydrophobic surfaces demonstrate the self-cleaning properties and have potential for liquid chemical sensing applications.

2. Experimental

2.1. Materials

The experiments detailed in this paper were performed on commercially available copper (purity 99.9%) and brass sheets (RS Components, CZ121M, 58% Cu, 39% Zn, and 3% Pb) with thicknesses of 0.45 and 0.6 mm, respectively. Prior to laser radiation, the samples were cleaned with isopropanol.

2.2. Surface laser irradiation

Hierarchical structures on the sample surface were fabricated using a SPI fiber laser (20 W EP-S) system including a galvanometer scanning system to move the beam over the surface as shown in Fig. 1 [25]. Arrays of microgroove structures were directly written on the sample surface. The distance between adjacent microgrooves (pitch size, d) was kept constant. The sample was irradiated, normal to the surface, by the fiber laser with nominal beam spot of about 21 μm, wavelength of 1064 nm and pulse width of ~220 ns. A scanning speed of 75 mm/s and repetition rate of 25 kHz were used. This processing rate is about two orders of magnitude higher compared with that using femtosecond lasers [16,18]. Three different fluences were applied separately to the work piece for copper (75, 84, 93 J/cm^2) and brass (55, 65, 75 J/cm^2).

2.3. Surface analysis

The samples were left in air, under ambient conditions before studying their surface wettability by measuring the contact angle. A ~5 μL droplet of deionized water was dispensed onto the sample surface using a syringe while an image was captured by a camera (Unibrain 1394) combined with a 12× magnification system. The contact angle (θ) was then determined by analyzing the droplet images using the software FTA32 (version 2.0). The contact angle hysteresis ($\Delta\theta$) was estimated by comparing the advancing and receding contact angle. The rolling-off angle was estimated as the tilted superhydrophobic surface on which deposited droplets start to rolling downwards. In order to study the surface morphology of the laser textured samples, scanning electron microscopy (SEM) and optical microscopy (Leica DM6000M) were used. The chemical composition of the surface was investigated by energy-dispersive X-ray (EDX) measurements.

2.4. Chemical solution for sensing demonstration

Methanol (99.5% purity) was dissolved in deionized water to form methanol solutions with various concentrations. ~5 μL droplets of these solutions were dispensed on laser textured brass surfaces that had previously been exposed to ambient conditions for 38 days. The contact angle was determined as described in Section 2.3.

3. Results and discussion

3.1. The effect of laser irradiation on surface structure

Prior to fabricating the microgroove structures, the effect of individual pulses on the surface was studied. Fig. S1 shows the near-circular craters induced on the copper surface by single pulses of laser radiation. The craters are formed due to the rapid heating of the copper, resulting in melting and evaporation (ablation), at the location of the laser radiation. Most of the material from the center of the crater was redeposited in the area surrounding the crater. The total amount of removed material depends on laser fluence. Fig. S1b–d shows the increase of crater diameter from about 24 μm under 75 J/cm^2 to 30 μm under 93 J/cm^2. The crater depth (determined by optical microscopy) also increased from around 4 to 6 μm, respectively. Similarly, Fig. S2 present craters on brass surface irradiated with three fluences. The crater diameter on brass increased from approximately 27 to 30 μm under fluence of 55 and 75 J/cm^2, respectively. The crater depth was around 3–5 μm.

Fig. S3 shows how microgroove structures can be created by increasing overlap of laser spot. The same scanning speed at 75 mm/s was applied while the repetition rate of the laser was varied from well separated pulses (Fig. S3a) to partly (Fig. S3b) and highly (Fig. S3c) overlapping. With a repetition rate of 25 kHz, the microgroove structure was formed with a significant amount of recast material around the perimeter of the feature. Fig. 2a shows a SEM image of the completed microgrooves on brass, irradiated with 65 J/cm^2, demonstrating the effect of the laser radiation on creating regular microstructures with micro-roughness on the sample's surface. Depth of the microgrooves on copper and brass surfaces, measured using optical microscopy, varied from around 10 to 25 μm, depending on laser fluence. Fig. 2b shows a three-dimensional image of the structure on brass surface irradiated with 65 J/cm^2 indicating that the depth of microgrooves was about 20 μm. It is noted that, due to high pulse overlap, the depth of the channels is larger than that of the craters created by a single pulse.

3.2. Time effects on surface wettability

The laser treated surfaces becomes hydrophilic immediately after fabrication (see Supporting Video 1 for more information). However, the surface wettability decreases over time, as indicated by the increase in contact angle. The first measurement after processing was made after the samples were left under ambient conditions for 3 days. Fig. 3 plots the evolution of contact angle with time for copper and brass samples with $d = 75$ μm, irradiated by three different fluences. Each data point presented is average value of three individual measurements. It can be seen that the contact angle exhibits a sharp increase during the first ten days, which then slows to a gradual growth before finally reaching a steady