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Superhydrophobic and colorful copper surfaces fabricated by picosecond laser induced periodic nanostructures

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ABSTRACT

In this study, functional copper surfaces combined with vivid structural colors and superhydrophobicity were fabricated by picosecond laser. Laser-induced periodic surface structures (LIPSS), i.e. ripples, were fabricated by picosecond laser nanostructuring to induce rainbow-like structural colors which are uniquely caused by the grating – type structure. The effects of laser processing parameters on the formation of ripples were investigated. We also discussed the formation mechanism of ripples. With different combinations of the laser processing parameters, ripples with various morphologies were fabricated. After the modification with triethoxyoctylsilane, different types of ripples exhibited different levels of wettability. The fine ripples with minimal redeposited nanoparticles exhibited high adhesive force to water. The increased amount of nanoscale structures decreased the adhesive force to water and increased the contact angle simultaneously. In particular, a specific type of ripples exhibited superhydrophobicity with a large contact angle of 153.9 ± 3.2° and a low sliding angle of 11 ± 3°.

1. Introduction

Thanks to the presence of surprisingly minute microstructures on their body surface, Morpho butterflies bear brilliant blue color on their wings; and the color of damselfish reversibly changes between green and blue [1,2]. In addition to these interesting structural colors, some creatures and plants in nature also exhibit extraordinary surface wettability due to the microstructures on their surface. For example, the lotus leaf shows self-cleaning property, and the rose petal shows superhydrophobicity combined with high adhesive force to water [3]. Inspired by nature, many methods have been used to induce surface micro/nano-structures on metals and thus to obtain surfaces with unusual optical properties or wettability [4–6]. Among these methods, laser nanostructuring using an ultrafast pulse laser source has been widely studied in recent years as it is a one-step direct maskless fabrication technique which can provide excellent flexibility [7–10]. Wu et al. have prepared stable superhydrophobic steel surface by femtosecond laser irradiation and subsequently coating them with trichlorosilane [11]. Vorobyev et al. have created a variety of colors on metals using femtosecond laser processing techniques [12]. However, there is a relative absence of studies on the application of ultrafast lasers to modify both the optical properties and wettability of metallic materials. Biomimetic metallic surfaces with both structural colors and superhydrophobicity have not been fabricated by ultrafast laser nanostructuring method.

In this study, we used a picosecond laser to fabricate large area laser-induced periodic surface structures (LIPSS), i.e. ripples, on copper surfaces. With suitable combinations of the laser processing parameters, ripples with different morphologies were fabricated and exhibited rainbow-like structural colors. Furthermore, we studied the wettability of the laser structured surfaces in detail. After the modification with triethoxyoctylsilane, different ripples exhibited different levels of wettability. In particular, some of these ripples exhibited superhydrophobicity with a large contact angle (153.9 ± 3.2°) and a low sliding angle (11 ± 3°). Successfully prepared copper surfaces showed similar characteristics as that of the wings of Morpho butterfly, namely the combined effects of superhydrophobicity and structural color. These functional surfaces may have potential applications in the field of bionics, decoration and so on [2,13].

2. Experimental

Copper samples (99.9% purity) with a dimension of 25 mm × 25 mm × 2 mm were polished mechanically and cleaned ultrasonically in ethanol before laser treatment.

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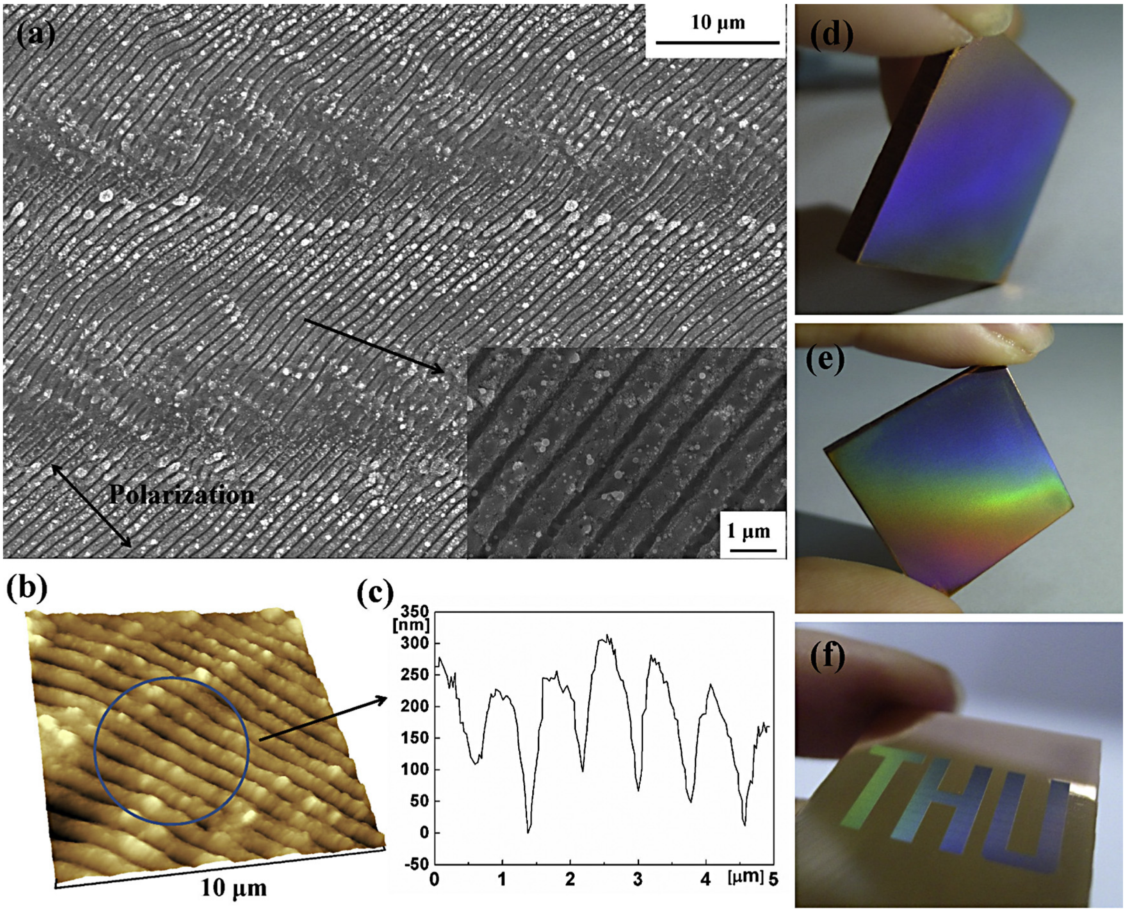

Fig. 1. (a) SEM micrograph of the copper surface irradiated by 509 pulses/irradiation spot. The average laser fluence was 0.43 J/cm^2. (b) 3D-AFM image of the sample. The scanned area was 10 μm × 10 μm. (c) The corresponding cross-sectional profile of (b). (d–f) Photographs of the large-area (25 mm × 25 mm) laser structured copper sample.

An Edgewave picosecond laser source with 1064 nm wavelength, 203.6 KHz repetition rate, and about 10 ps pulse width was used in our experiments. The direction of the laser polarization vector was changed by a half wave plate. A two mirror galvanometric scanner (hurrySCANII14) with an F-Theta objective lens (f = 100 mm) was used to focus and scan the laser beam in the x–y direction. The diameter of the focused spot at $1/e^2$ of the maximum intensity of the Gaussian profile of the laser beam was approximately 25 μm as analyzed by a beam analyzer (SPIRICON). A power meter (LabMax Top from Coherent) was used to measure the average power of the laser beam. Lastly, the lateral overlap rate in our experiments was 20%. All the laser treatments were performed in ambient atmosphere under normal incidence of the laser beam.

Following laser nanostructuring, the samples were cleaned with compressed air and then were immersed in 5 mM ethanolic triethoxyoctylsilane (molecular formula: $CH_3(CH_2)_7Si(OC_2H_5)_3$ from Sinopharm) solution for 1 h at room temperature followed by washing with ethanol and drying in an oven at 80 °C for 20 min.

The morphology of the laser structured surfaces was studied using a LEO-1530 scanning electron microscope (SEM) in secondary electron imaging mode with an acceleration voltage of 10 kV. The topography was investigated with a SPM-9600 atomic force microscope (AFM) in contact mode. Profile measurements were performed for five times for each AFM image. The average surface roughness (R_a) was determined by a 3D optical profilometer (MicroXAM-3D, ADE technology) with 1 nm resolution in vertical direction. X-ray photoelectron spectroscopy (XPS) analysis was used to quantify the elemental composition of the surface. The wettability of the samples was evaluated by measuring the contact angle (CA) and sliding angle (SA) with a video-based optical contact angle measuring device (OCA 15 plus from Data Physics Instruments). The sessile drop technique and the tilting plate method were used for the measurement of contact angles (CAs) and sliding angles (SAs), respectively. The selected water droplet volume was 3 μL. The CA and SA of the water droplet on each sample surface were measured for five times, and three samples were analyzed per group. All measurements were performed when the droplets reached stability.

3. Results and discussion

3.1. Ripples formation

Fig. 1a shows the typical SEM micrograph of the ripples formed with an average laser fluence of 0.43 J/cm^2. The number of laser pulses per irradiation spot was 509. By continuously scanning step by step, the adjacent laser tracks were partially overlapped to each other and formed continuous long ripples perpendicular oriented to the linear polarization vector of the laser beam. Fig. 1b shows a 3D-AFM image of the ripples. Ripples with a significantly smaller spacing than the irradiation laser wavelength (1064 nm) were observed. The corresponding cross-sectional profile is shown in Fig. 1c. Evidently, the periodic surface structure has a very clear contour with an average spatial periodicity of 750 ± 31 nm. The average height of the ripples was 270 ± 22 nm. As shown in Fig. 1d and e, large-area uniform samples exhibited various colors at different viewing angles, which can be attributed to the unique effect of grating – type structure. Due to the flexibility of the laser surface

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