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Fabrication of long-term stable superoleophobic surface based on copper oxide/cobalt oxide with micro-nanoscale hierarchical roughness

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ABSTRACT

We have demonstrated a simple and cost-effective technique for the large-area fabrication of a superoleophobic surface using copper as a substrate. The whole process included three simple steps: First, the copper substrate was oxidized under hot alkaline conditions to fabricate flower-like copper oxide microspheres by heating at a particular temperature for an interval of time. Second, the copper-oxide-covered copper substrate was further heated in a solution of cobalt nitrate and ammonium nitrate in the presence of an ammonia solution to fabricate cobalt oxide nanostructures. We applied this second step to increase the surface roughness because it is an important criterion for improved superoleophobicity. Finally, to reduce the surface energy of the fabricated structures, the surfaces were chemically modified with perfluorooctyltrichlorosilane. Contact-angle measurements indicate that the micro–nano binary (MNB) hierarchical structures fabricated on the copper substrate became super-repellent toward a broad range of liquids with surface tension in the range of 21.5–72 mN/m. In an attempt to significantly improve the superoleophobic property of the surface, we also examined and compared the role of nanostructures in MNB hierarchical structures with only micro-fabricated surfaces. The fabricated MNB hierarchical structures also displays thermal stability and excellent long-term stability after exposure in air for more than 9 months. Our method might provide a general route toward the preparation of novel hierarchical films on metal substrates for various industrial applications.

1. Introduction

Superhydrophobic surfaces have gained great importance because of their potential applications in diverse fields such as self-cleaning [1–5], anti-icing [6–8], oil–water separation [9–12], corrosion resistance [13–15], drag reduction [16,17], antifouling technologies [18,19], etc. By recognizing the roles of the two key parameters, surface energy and roughness, researchers have developed artificial surfaces with superhydrophobic properties using a variety of methods including etching [20–23], sol–gel process [24], electrospinning [25], deposition of nanoparticles on smooth or rough substrates [26], growth of nanotubes [27], electrochemical anodization [28], and laser fabrication [29]. In particular, the substrate roughness and the chemical composition of the coating determine the surface free energy (SFE) and play a very important role in achieving superhydrophobicity. For a given material, it is possible to lower the SFE of the superhydrophobic coating by suitably modifying the surface morphology of the substrate.

Recently, superoleophobic surfaces that can repel essentially any oil, including various low-surface-tension liquids, have attracted much attention because of their importance in both research and industry. A surface is considered superoleophobic if the apparent contact angle θ^* for the contacting liquid droplet is greater than 150° and the surface displays a low sliding angle. Superoleophobic substrates are used in various industrial applications such as fluid transfer, fluid power systems, stain-resistant or antifouling coverings. Compared to superhydrophobic surfaces, however, it is difficult to prepare superoleophobic surfaces that resist wetting with low-surface-energy oils. Many research groups have tried various techniques to create superoleophobic surfaces and some promising results have been reported [30–34]. By controlling both the surface energy and morphology, which are the two key surface parameters that govern the wettability of solid surfaces, artificial superoleophobic surfaces can be fabricated. Recent reports indicate that a dual-scale roughness (i.e., micrometer-scale and nanometer-scale surface roughness) significantly enhances the

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superhydrophobic and superoleophobic property [35,36]. In order to create the dual-scale roughness, various techniques such as lithography, chemical etching, plasma etching, and laser treatment have been used by researchers.

In consideration of the effect of surface roughness, two models have been developed: the Wenzel model [37] and the Cassie–Baxter model [38]. In the Wenzel state, the contacting liquid droplet completely permeates the surface protrusions, forming the so called "fully-wetted" interface. In the Cassie–Baxter state, the drop rests on the rough surface and does not completely wet the surface texture because of the air pockets that remain trapped underneath the hierarchical microstructures and nanostructures. It has been established that the increase in surface roughness in the form of microstructures and nanostructures reduces the apparent SFE owing to the reduced contact area between the liquid droplet and the fabricated surface. Thus, for practical applications, it is important to modify the substrate with the desired roughness in order to obtain a superoleophobic surface.

As an important engineering material, copper is widely used in many industrial applications. Up to now, there have been different reports on the fabrication of artificial superhydrophobic copper surfaces [39–45]. Recently, superoleophobic copper substrates have received much attention and researchers have reported a few methods for their development [46–49]. Zhang et al. [46] fabricated a hierarchical superamphiphobic (i.e., superhydrophobic and superoleophobic) structure composed of nanorod arrays and microflowers using an alkali-assisted oxidation process on a copper sheet. After fluorination, the surface became super-repellency toward several organic liquids. They also checked the stability of the created superamphiphobic surface with the compression and immersion test. Li et al. [47] recently fabricated superoleophobic surfaces on a copper substrate by combining a two-step surface-texturing process. The results showed that spherical micropits with diameters of $50-100\,\mu$m was formed in the first step of surface texturing; in the second step, $Cu(OH)_2$ or CuO with structures of nanorods, microflowers, or microballs was formed. They also demonstrated that the UV and oxidation resistance of the fabricated surface remained stable for a period of 10 days. Some methods mentioned in the literature are very simple and can be applied in industrial applications. But in most of the reports, the authors did not discuss the long-term stability of the fabricated surfaces under atmospheric conditions, which we believe is an important issue in terms of practical applications. Moreover, the authors examined the superoleophobic property mostly with oils that have surface tension $\geq$25 mN/m, such as rapeseed oil (35.7 mN/m) or hexadecane (27.5 mN/m).

In our current work, we fabricated superoleophobic copper substrates with both micrometer-scale and nanometer-scale binary (micro–nano binary or MNB) hierarchical structures that displays high contact angle (CA) and low sliding angle (SA) for different liquids. The entire process includes three simple steps: First, the copper substrate is oxidized under hot alkaline conditions to produce copper oxide with flower-like microspheres by heating at a particular temperature for a specific interval of time. Second, the copper substrate with copper oxide grown on the surface is further heated in a solution of cobalt nitrate and ammonium nitrate in the presence of an ammonia solution to produce cobalt-oxide nanostructures. This second step serves to increase the surface roughness in order to obtain superoleophobicity. Finally, the surfaces are chemically modified with perfluorooctyltrichlorosilane (PFOTS) to reduce the surface energy of the fabricated structures. This is a unique method to generate both superhydrophobic and superoleophobic conditions on the same copper plate. Our fabricated superoleophobic surface exhibited better results even for liquids with extremely low surface tension, such as hexadecane (27.5 mN/m) and silicone oil (21.5 mN/m). Furthermore, we also investigated the role of nanostructures in an attempt to significantly improve the superoleophobic property of the fabricated surface. The fabricated superoleophobic copper substrates also exhibited better thermal stability and long-term stability in air.

2. Experimental

2.1. Materials

Copper substrates (20 mm × 20 mm × 1.27 mm, purity 99.9 wt%), ammonium hydroxide, cobalt nitrate, ammonium nitrate, and 1*H*,1*H*,2*H*,2*H*-perfluorooctyltrichloro-silane (PFOTS) were obtained from Alfa Aesar, Inc. Other chemicals were of analytical grade and used without further purification.

2.2. Synthesis of copper-oxide structures

First, the copper plates was ultrasonically cleaned with acetone followed by ethanol solution for 5 min each, then rinsed three times with deionized water to remove surface impurities, and dried. After drying under a N_2 flow, the copper plates was immersed in a sealed glass bottle (250 mL) containing a 0.03 M NH_4OH solution and heated in an oven at 60 °C for 42 h. The samples were then rinsed with deionized water and dried at room temperature. A uniform, dark black film was deposited on the copper substrate, indicating the formation of an oxide layer.

2.3. Synthesis of cobalt oxide structures

The cobalt-oxide nanoparticles was synthesized by an ammonia-evaporation-induced method. Typically, 10 mmol of $Co(NO_3)_2$ and 5 mmol of NH_4NO_3 were dissolved in 15 mL of a 30 wt% ammonia solution and 35 mL of H_2O. The homogeneous solution was magnetically stirred for 0.5 h in air, during which the original pink color gradually turned to black. The solution was then transferred to a covered Petri dish containing the copper substrate with the copper oxide grown on its surface and heated in an oven at 90 °C for 12 h.

Finally, to reduce the surface energy on the fabricated structures, the surfaces of the as-prepared samples was chemically modified with PFOTS. The samples was immersed in 1% PFOTS in hexane at 100 °C for 1 h on a hot plate (Scheme 1).

2.4. Sample characterization

The morphology of all the samples prepared in the present study was examined using field-emission scanning electron microscopy (FESEM; JSM-7610F, JEOL, Japan). The CA and SA was measured with 5 μL droplets of water and various oils using a CA measurement system (Phoenix 300 Touch, SEO Co., Ltd., South Korea). The average CA and SA values was obtained by measuring each sample at a minimum of five different positions at room temperature. The value of the CA was calculated using the tangent line method. The surface roughness was measured using surface profilometer (KLA-Tencor company, Model No. P 10, USA). The crystal structure of the fabricated samples was examined using an X-ray diffractometer system (XRD) using a Bruker D8 Advanced with Cu Kα radiation at 40.0 kV and 40.0 mA. The samples were scanned at $2^\circ\theta$ range from 30° to 70°. The optical images of the droplets were obtained using a digital camera (Sony Inc., Japan).

3. Results and discussion

3.1. Fabrication

To obtain a superoleophobic surface, a suitable rough surface is essential. In this work, copper metal was the preferred substrate