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Superamphiphobic CaLi-based bulk metallic glasses

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A superamphiphobic (both superhydrophobic and superoleophobic) CaLi-based bulk metallic glass (BMG) surface was constructed by etching the surface with water and modifying the etched surface with fluoroalkylsilane coating. The modified surface exhibits high corrosion resistance and stable superamphiphobicity with a high static contact angle of more than 150°; these properties could extend the practical applications of BMGs. The superamphiphobicity mechanism of the BMG is discussed. The facile method can be used to form other BMG surfaces with special wettability.

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Recently, increasing numbers of metallic glasses in bulky form have been fabricated [1–4]. These bulk metallic glasses (BMGs) exhibit outstanding physical, mechanical and chemical properties, which make them attractive for engineering applications [5–11]. However, attention has mainly been focussed on the fabrication of BMGs and the investigation of their mechanical and magnetic properties, and little work has been devoted to studying the surface behavior of BMGs. In fact, the surface of a material, including traditional glasses, plays an important role in the performance of the entire system in practical application. The atomic structure and bonding of glassy alloys are completely different from those of crystalline alloys, which could result in different surface behaviors [5,6]. Generally speaking, the glassy alloys have better corrosion resistance compared to their crystalline counterparts, while some BMGs based on active elements such as Mg, Ca and rare earth elements have unique properties but poor corrosion resistance [6,8]. Therefore, to maximize the utility of the BMGs, it is essential to develop simple and effective methods to improve their corrosion resistance.

Wettability is an important property of a solid surface and plays an important role in daily life, industry, agriculture and biological processes, such as the prevention of the adhesion of snow to antennas and windows,

self-cleaning traffic indicators, the reduction of frictional drag on ship hulls, metal refining, stain-resistant textiles and cell motility [12]. In nature, the surface of lotus leaves are covered with a simple epicuticular wax and have a special surface morphology, resulting in superhydrophobic properties: the contact angle of water beads on lotus leaves is as large as about 160°. Particles of dirt can be removed by water droplets that roll off the surfaces independent of the chemical nature or size of these particles. This is the so-called “lotus effect”.¹³ Because they are important in a range of applications, superhydrophobic or superoleophobic surfaces have attracted much attention recently, and attempts to mimick these behaviors have been exploited [13–18]. Generally, the wettability of solid substrates is governed by their surface free energy and surface geometrical structure. Therefore, dynamically changing one of these two factors can modulate surface wettability [19–25].

In this paper, we present a simple and feasible method for the construction of stable superhydrophobic and superoleophobic BMG surfaces. Inspired by biomaterials, the synthetic strategy consists of forming micro-nano-scale hierarchical surface structures and then modifying the surface using ultrathin fluoroalkylsilane (FAS) with low surface energy. The obtained BMG surface presents dramatically improved corrosion resistance and highly stable superamphiphobic properties.

The newly discovered $\text{Ca}_{65}\text{Li}_{10}\text{Mg}_{8.5}\text{Zn}_{16.5}$ BMG was chosen as our samples. This BMG has good glass-forming ability and unique properties (such as ultralow

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elastic moduli (Young's modulus is about 23.0 GPa), low glass transition temperature (44 °C), lowest density (1.956 g cm^{-3}) of all BMGs, ultrahigh specific strength and polymer-like thermoplastic formability near room temperature), has potential for practical applications, and facilitates studies of the nature of glasses [8]. However, BMGs with active elements Ca and Li as dominant components have poor oxidation and corrosion resistances. To prepare the superhydrophobic surface, the CaLi-based BMG sheets were firstly ultrasonically cleaned in acetone. After drying in air, the sheets were soaked in double-distilled water for several minutes. The BMGs were etched by water as this can dissolve the glass. The sample surface was then rinsed with acetone, dried in air, modified with a 1.0% ethanol solution of FAS ($\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$) for 12 h, and subsequently dried in air. The contact angle was measured using a Dataphysics OCA20 contact angle system.

The shape of a water droplet on the untreated BMG surface is shown in Figure 1a, which demonstrates the hydrophilic property of the untreated BMG sample. Figure 1b and c present a water droplet and an oil droplet, respectively, on the BMG surface modified with FAS: the water droplet and the oil droplet are perfectly spherical in shape, riding on top of the BMG surfaces, indicating the superhydrophobic and superoleophobic properties. The water and oil contact angles are

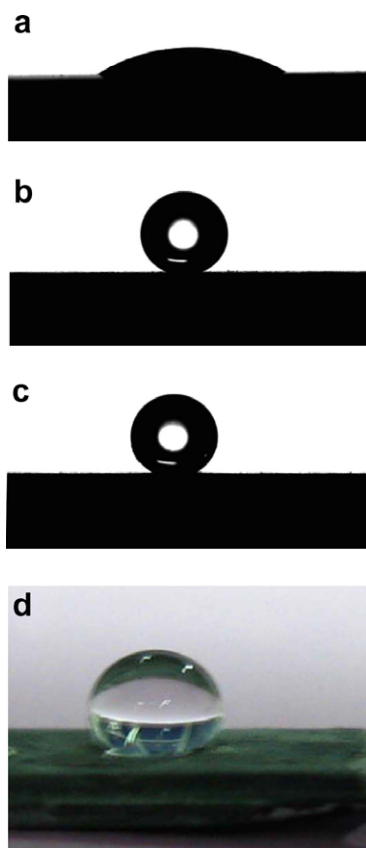


Figure 1. Droplets shapes on the surfaces of CaLi-based BMGs. (a) Water droplet shape on the untreated BMG surface. (b) Water droplet shape on the treated BMG surface. (c) Oil droplet shape on the treated BMG surfaces. (d) Photographic image of a water droplet on the treated BMG surface after exposure to air for three months.

$162 \pm 2^\circ$ and $156 \pm 3^\circ$, respectively. Furthermore, the water droplets are hardly able to stick to the modified BMGs surfaces, and rolled off quite easily. We scattered some metallic powder on the BMG surface, and the rolling water droplets were able to pick these up easily: the BMG surface thus exhibits a self-cleaning effect, resembling the lotus effect. Meanwhile, the modified BMG presents long-term stable corrosion resistance. Even after exposure to ambient atmospheric conditions for more than three months, the surface of the BMG modified with FAS still maintains its original color superamphiphobicity. Figure 1d shows a photograph of a water droplet (about 7 mg) sitting on a treated BMG surface that had been exposed to air for more than three months. This water droplet is spherical in shape, which indicates that the BMG modified with FAS possesses stable superhydrophobicity and good corrosion resistance. It should be noted that, under the same experimental condition, the untreated surfaces of BMG are severely oxygenated within 1–2 weeks and their surface color becomes black.

The composition of the CaLi-based BMG surface after FAS modification was characterized by X-ray photoelectron spectroscopy (XPS) and the result is shown in Figure 2. The XPS spectrum clearly shows C, O, F and Si components on the surfaces, indicating that the surface of the glass has been fully covered by the FAS film. The FAS coatings can serve as a barrier against a hostile environment. For instance, CaLi-based BMGs are highly susceptible to attack by water and other chemicals and to oxidation. For unmodified BMGs, droplets of water or dilute HCl aqueous solution on their surfaces can cause drastic oxidation and severe corrosion. However, modified BMGs, in contrast to untreated ones, are well preserved under ambient conditions even for long periods. The corrosion resistance of the BMG is significantly improved after surface treatment with FAS film. The FAS film, which has a low surface energy, can also lead to hydrophobic or oleophobic surfaces. In order to explain the superamphiphobicity displayed by the BMG surface, its surface morphology must be considered.

Surface roughness plays an important role in determining the wetting behavior of a solid surface, and an appropriate increase in the surface roughness of hydro-

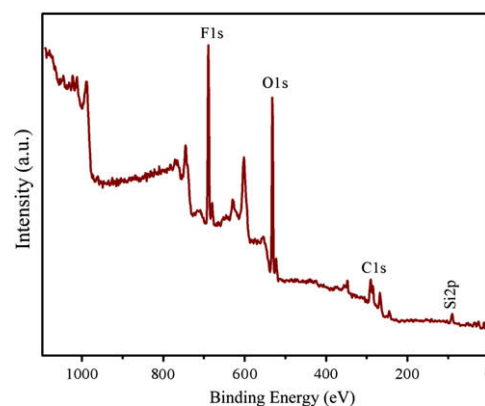


Figure 2. XPS (Al K_α) spectra of the superamphiphobic CaLi-based BMG surface.

phobic materials can dramatically enhance surface water repellency [13–18]. Scanning electron microscopy (SEM) images at different magnifications of the BMG surfaces before and after treatment are shown in Figure 3. Before treatment, the BMG surface is flat with only a few impurities (smaller than 1 μm) scattered on it (Figure 3a and b). After treatment, the BMG surface becomes misshapen. The SEM image (Figure 3c) shows rugged surfaces with irregular grooves on the micron scale. The SEM picture at high resolution shows a coral-like pattern on the BMG surface (Figure 3d). It can be seen that small protrusions aggregate on the micrometer-level configurations with some rod-like outshoots on top. The densely packed protrusions have a wide diameter distribution, with an average size of about 100 nm. The treated BMG surface actually has micro-nano-scale hierarchical structures, which dramatically increase the surface roughness.

The wettability of solid surfaces is influenced by both the surface morphology (surface roughness) and the chemical composition [18–26]. To explain the mechanism, we introduce the Cassie–Baxter equation [17,18]: $\cos \theta^* = -1 + \phi_s(\cos \theta + 1)$, where θ^* and θ represent the water contact angles on rough and smooth surfaces, respectively; ϕ_s is the fraction of the surface that is in contact with liquid, and the remaining fraction, $1 - \phi_s$, is in contact with air. Low surface energy (corresponding to large θ) and rough surface (corresponding to small ϕ_s) would give a large θ^* , which corresponds to hydrophobicity. On the BMG surface, small ϕ_s values are achieved by introducing air cavities on the surface via etching. The presence of the binary micro-nano-scale hierarchical structure dramatically increases the surface roughness of the BMG surface, which greatly minimizes the contact area between water droplets and the BMG surface. On the other hand, large θ values are achieved via low surface energy FAS coating. Both the micro-nano-scale hierarchical structures and FAS coating result in the stable superhydrophobic and superoleophobic states.

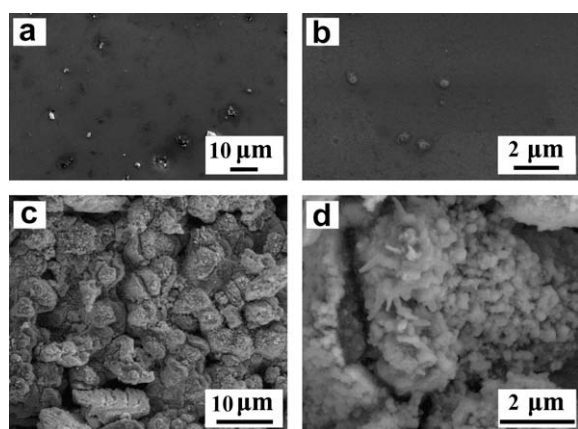


Figure 3. SEM image of the CaLi-based BMG surface. (a) Low-magnification SEM image of the surface before treatment. (b) High-resolution SEM image of the surface before treatment. (c) Low-magnification SEM image of the surface after treatment. (d) High-resolution SEM image of the surface after treatment.

In summary, by using a facile water etching and chemical coating method, BMG surfaces with binary micro-nano-scale hierarchical structures coated with FAS film have been constructed. Due to the combination of the surface roughness and the low surface free energy FAS, the resultant BMG surface exhibited stable superhydrophobic and superoleophobic properties and improved corrosion resistance, which may extend the practical applications of BMG material. We expect this facile method can be widely used for the construction of other BMG surfaces with special wettability through selection of suitable solvents.

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- [1] D.C. Hofmann, J.Y. Suh, A. Wiest, G. Duan, M. Lind, M.D. Demetriou, W.L. Johnson, *Nature* 451 (2008) 1085.
- [2] Y.H. Liu, G. Wang, R.J. Wang, M.X. Pan, W.H. Wang, *Science* 315 (2007) 1385.
- [3] B. Zhang, D.Q. Zhao, W.H. Wang, A.L. Greer, *Phys. Rev. Lett.* 94 (2005) 205502.
- [4] M.B. Tang, D.Q. Zhao, M.X. Pan, W.H. Wang, *Chin. Phys. Lett.* 21 (2004) 901.
- [5] M.W. Chen, *Annu. Rev. Mater. Res.* 38 (2008) 445.
- [6] W.H. Wang, *Prog. Mater. Sci.* 52 (2007) 540; W.H. Wang, *J. Appl. Phys.* 99 (2006) 093506.
- [7] O.N. Senkov, D.B. Miracle, V. Keppens, P.K. Liaw, *Metal. Mater. Trans. A* 39 (2007) 1888.
- [8] J.F. Li, D.Q. Zhao, M.L. Zhang, W.H. Wang, *Appl. Phys. Lett.*, in press.
- [9] G.F. Ma, H.F. Zhang, H. Li, Z.Q. Hu, *Appl. Phys. Lett.* 91 (2007) 181905.
- [10] G. Kumar, J. Schroers, *Appl. Phys. Lett.* 92 (2008) 031901.
- [11] Q. Luo, D.Q. Zhao, M.X. Pan, W.H. Wang, *Appl. Phys. Lett.* 89 (2006) 081914.
- [12] H.Y. Erbil, A.L. Demirel, Y. Avci, O. Mert, *Science* 299 (2003) 1377.
- [13] W. Barthlott, C. Neinhuis, *Planta* 202 (1997) 1.
- [14] L. Zhai, F.C. Cebeci, R.E. Cohen, M.F. Rubner, *Nano Lett.* 4 (2004) 1349.
- [15] K. Liu, M. Zhang, J. Zhai, J. Wang, L. Jiang, *Appl. Phys. Lett.* 92 (2008) 183103.
- [16] S. Wang, L. Feng, L. Jiang, *Adv. Mater.* 18 (2006) 767.
- [17] A.B.D. Cassie, S. Baxter, *Trans. Faraday Soc.* 40 (1994) 546.
- [18] J. Genzer, K. Efimenko, *Biofouling* 22 (2006) 339.
- [19] L. Feng, S.H. Li, Y.S. Li, H.J. Li, L.J. Zhang, J. Zhai, Y.L. Song, B.Q. Liu, L. Jiang, D.B. Zhu, *Adv. Mater.* 14 (2002) 1857.
- [20] T.L. Sun, L. Feng, X.F. Gao, L. Jiang, *Acc. Chem. Res.* 38 (2005) 644.
- [21] X. Zhang, F. Shi, J. Niu, Y.G. Jiang, Z.Q. Wang, *J. Mater. Chem.* 18 (2008) 621.
- [22] X.J. Feng, L. Jiang, *Adv. Mater.* 18 (2006) 3063.
- [23] P. Roach, N.J. Shirtcliffe, M.I. Newton, *Soft Matter* 4 (2008) 224.
- [24] M. Callies, D. Quere, *Soft Matter* 1 (2005) 55.
- [25] G. Palasantzas, J.Th.M. De Hosson, *Acta Mater.* 48 (2000) 3641.
- [26] X.B. Zhou, J.Th.M. De Hosson, *J. Mater. Res.* 10 (1995) 1984.