Non-destructive production of natural environment-adaptive super-hydrophobic hierarchical ceramic surface on a steel substrate

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A super-hydrophobic ceramic surface with excellent adaptability to the natural environment was developed on a metal substrate through a facile electrophoretic deposition approach. Alumina, as a demonstrating low cost ceramic material, was electrophoretically deposited on a steel surface to form a hierarchical surface structure. After the treatment with stearic acid, the as-fabricated surface exhibits a high water contact angle and very low sliding angle, revealing a super hydrophobicity. Furthermore, the surface can maintain the super hydrophobicity with liquids of different pH values, performing good natural environment adaptability.

1. Introduction: The surfaces with a very high water contact angle (CA) of −150° and a low sliding angle (SA) (<10°) are generally known as super-hydrophobic surfaces. These surfaces have attracted much research and industrial interests due to their potential applications, such as self-cleaning [1–9], anti-frosting [10, 11], fluid drag reduction [12, 13], oil and water separation [14–18], anti-reflection [19], microdroplet transportation [20] and so on. A super-hydrophobic surface can be attained by mimicking the hierarchical structure of lotus leaves.

Metals are widely used in various industrial and architectural fields as basic materials for numerous mechanical components. For this reason, a super-hydrophobic metal surface has many application possibilities by protecting the metal materials from the rain water. Many methods for fabricating super-hydrophobic metal surfaces have been reported. For example, Cho *et al.* [21] proposed a fabrication process for dual-scale hierarchical structures combining both microstructure via sand blasting techniques and the nanostructured aluminium hydroxide layer. In Wang's research [22], the electrodeposited Cu sample was thermally oxidised at 350°C in air for 1 h to fabricate CuO nanowires, which produced hierarchical structure of super-hydrophobic surface. Very recently, Joung and Buie [23] reported micro and nanostructured surfaces produced by adding SiO_2 nanoparticles to obtain super-hydrophobic property. Furthermore, a combination of layer-by-layer assembly and electrophoretic deposition of hydrophobic nanoparticles was also proposed to prepare a super-hydrophobic surface. However, up to now, the fabrication of natural environment-adaptive and stable super-hydrophobic surface in large scale is still a great challenge [24].

In this Letter, we report the production of low cost super-hydrophobic surface by electrophoretic deposition of a ceramic material (i.e. Al_2O_3) on a metal (i.e. steel) substrate. The prepared Al_2O_3 hierarchical surface exhibits a CA of −150° and a very low SA (<3°). In addition, the surface maintains the super hydrophobicity with the liquids of different pH values, demonstrating satisfactory natural environment adaptability.

2. Experimental details: Industrial grade stainless steel sheets ($60 \times 20 \times 2$ mm, 1Cr18Ni9Ti, Taigang, China) with different surface conditions such as a polished state and an abrasive blasted state, were used as a typical metal substrate material. Submicrometer-sized alumina powders (AMS-90B, Sumitomo Chemical, Japan) with a mean particle size of 0.7 μm were

dispersed in ethanol with a concentration of 8 g/L (Fig. 1). Polyethylene glycol with a mass fraction of 1% was added into the Al_2O_3 ethanol suspension as dispersant. Then, the suspension was ultrasonically dispersed for 30 min and magnetically stirred for 30 min. Next, electrophoretic deposition of submicrometer Al_2O_3 was carried out in this suspension on the steel substrate surface. During the electrophoretic deposition, the voltage was 60 V, and the deposition duration was 30 s. The pretreated stainless steel sheets were used as the cathode while another stainless steel sheet without surface treatment was used as the anode. Finally, the specimen was dipped in a stearic acid in ethanol solution with a concentration of 20 g/L at 50°C for 10 min and then dried at 80°C for 30 min. After the self-assembled monolayer coating with stearic acid was applied on the specimen, the as-developed hierarchical surfaces were subjected to the super-hydrophobicity measurements.

The static CA and SA on the fabricated surface were measured with an optical CA measuring device (JC2000C4, POWEREACH, China). A 5 μL of distilled water (or water with different pH values) droplet was used for this measurement. The CA results were averaged over at least five measurements (with a stabilisation
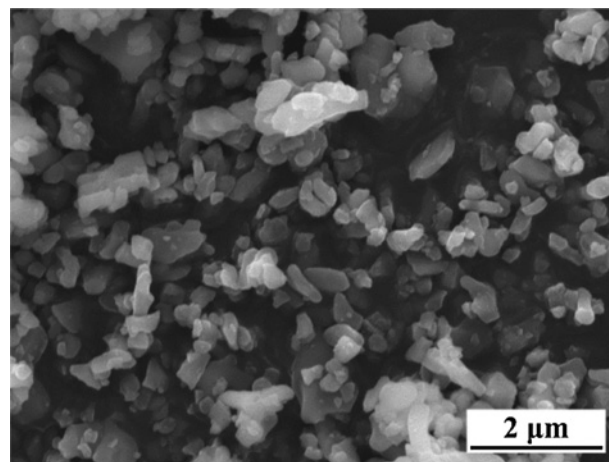

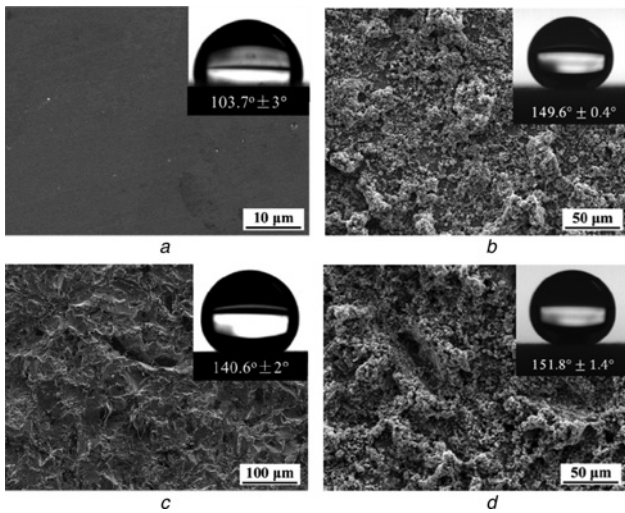**Fig. 1** *Morphology of submicrometer-scaled Al2O3 powder*

Fig. 2 *Surface morphologies of the substrates*
a Surface morphologies observed on the polished steel
b Electrophoretic deposition of Al_2O_3 on the polished steel
c Abrasive blasted steel
d Electrophoretic deposition of Al_2O_3 on the abrasive blasted steel. The insets in the figures *a–d* show the CAs for the corresponding surfaces

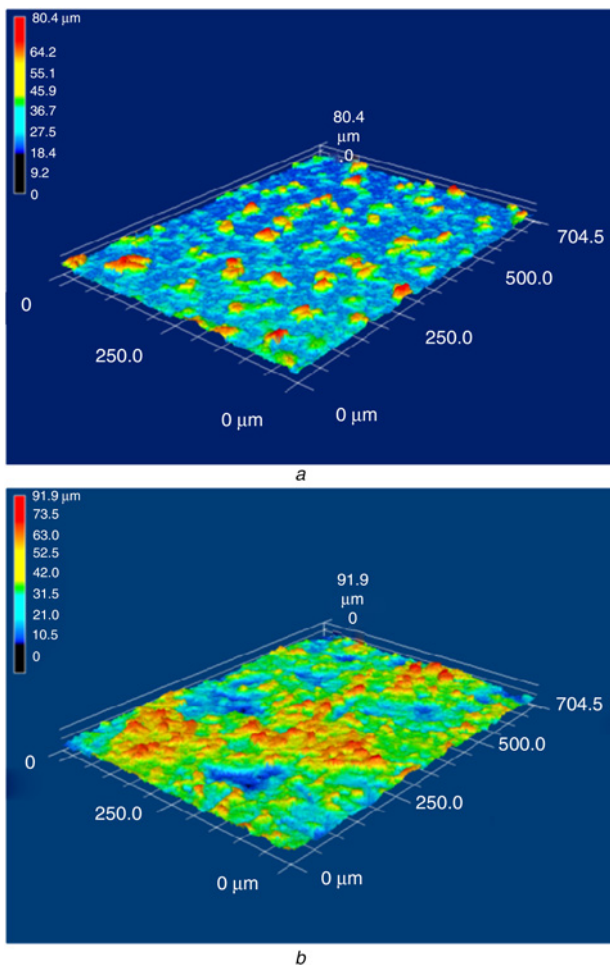time of 1 min after the droplet loading on the surface) on different locations of each specimen at room temperature.

Fig. 3 *Representative 3D LSCMs of the deposit surfaces of the submicrometer Al_2O_3 on*
a Polished steel substrate
b Abrasive blasted steel substrate

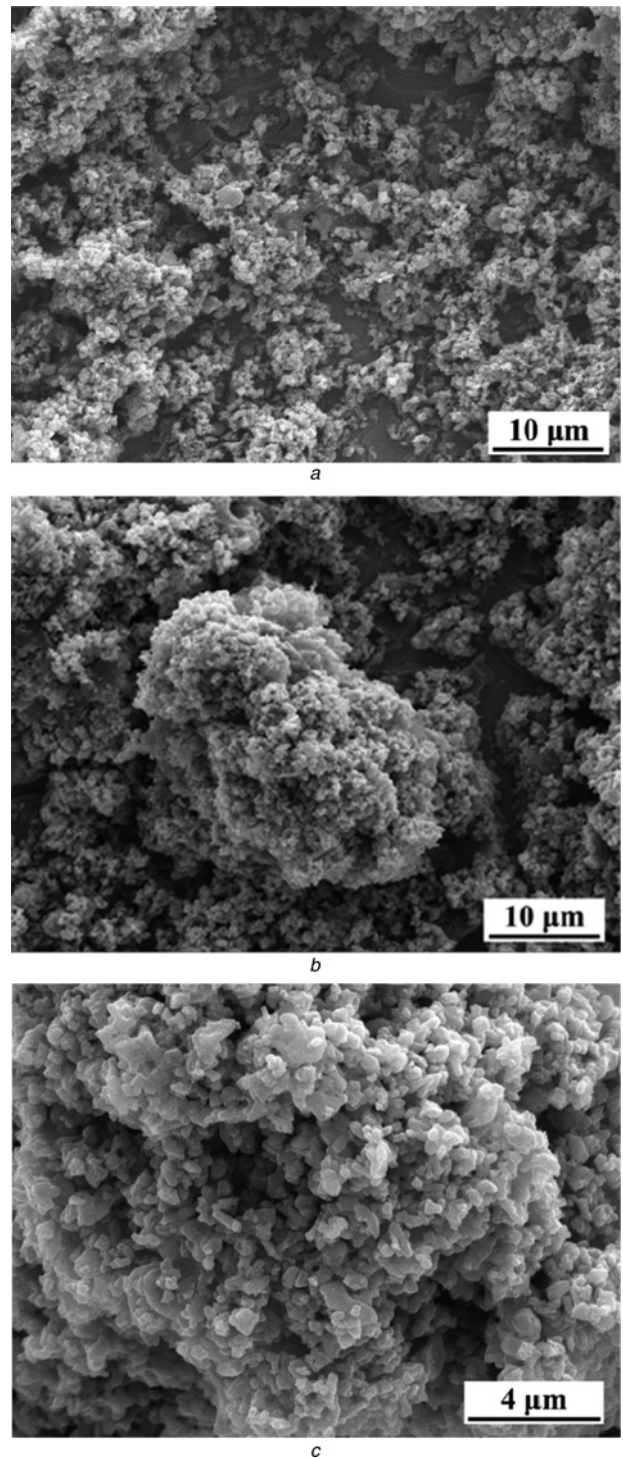**Fig. 4** *SEM images of the deposit surfaces on the polished steel substrate with various magnifications*
a Morphology of a relatively flat surface as shown in Fig. 2*b*
b Morphology of a rough surface with large nodulations as shown in Fig. 2*b*
c Magnified view as shown in Fig. 4*b*

The surface morphology was examined through scanning electron microscopy (SEM, VEGA II-XMU, TESCAN, Czech) and 3D Laser scanning confocal microscopy (LSCM, VK-9700K/VK-8700K, KEYENCE, Japan).

3. Results and discussion

3.1. Hierarchical surface morphology and hydrophobicity: Fig. 2 shows the surface morphologies of the substrates (i.e. polished steel and blasted steel) before and after the electrophoretical

deposition of alumina. Compared with the polished steel surface as shown in Fig. 2a, the alumina deposited surface on the polished steel, as shown in Fig. 2b, presents a quite rough surface morphology. In contrast, the blasted steel shows a much rougher surface compared with the polished steel, as revealed in Fig. 2c. While after the alumina deposition, the blasted steel substrate shows a more rough surface morphology, which can be clearly distinguished as shown in Fig. 2d.

To quantitatively characterise the topography of the deposit surfaces, 3D LSCM was employed. From the deposit surface on the polished steel substrate as shown in Fig. 3a, some microsized convexes in addition to the small submicrosized surface roughness can be distinguished. These two types of convexes on the steel surface can be attributed to the alumina particles electrophoretically deposited on the steel surface. In contrast, the deposit surface on the abrasive blasted steel substrate presents more microsized convexes, as shown in Fig. 3b.

To further reveal the morphology difference between the two deposit surfaces, the surface morphologies of the deposit surface of the submicrometer Al_2O_3 on the polished steel substrate with higher magnifications are shown in Fig. 4. Compared with the relatively flat surface shown in Fig. 4a, the convexes shown in Fig. 4b can be attributed to the large size agglomeration of the submicrosized alumina particles, and Fig. 4c clearly reveals the primary submicrosized alumina particle morphology. Furthermore, Fig. 4c also reveals that the deposited alumina particles have a size of several hundreds of nanometres. These alumina particles agglomerate to
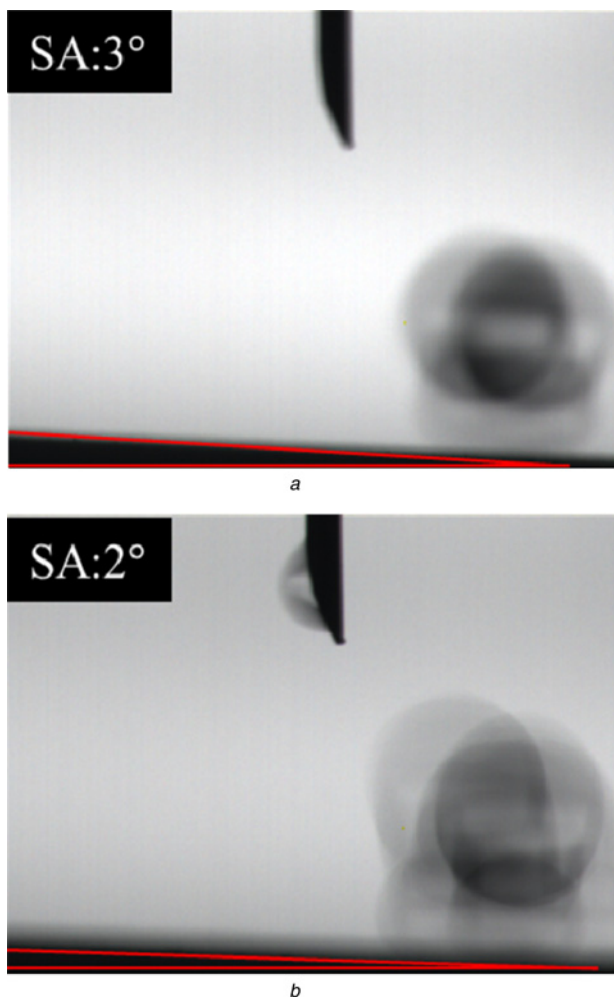
create a hierarchical surface morphology. Interestingly, the microsized convexes on the blasted steel surface can also increase the microsized convexes on the electrophoretically deposited surface, as evidenced from Figs. 2c and d. In brief, the changes in the surface morphologies after the electrophoretic deposition process indicate that the electrophoretic deposition of the submicrometer alumina can construct a hierarchical structure successfully on a metal substrate surface no matter it is smooth or rough.

The hydrophobicity of the various surfaces was examined by CA measurements. The CAs of the polished stainless steel and the abrasive blasted stainless steel are ca. $103.7° \pm 3°$ and $140.6° \pm 2°$, respectively, as shown in the insets of Figs. 2a and c. It means that the surface roughening by the abrasive blasting improves the CA. A similar phenomenon was reported in the literature [25, 26]. Actually, this abrasive blasting approach can be used for the large steel structures such as oil/gas pipes. However, the metal surface structure would be also changed by adding some intensively deformed structure and thereby degrading the fatigue resistance and service lifetime of these steel structures. After the electrophoretic deposition of the submicrometer Al_2O_3 and the modification with stearic acid, the CAs increase to ca. $150°$. In addition, the SAs decrease to about $3°$, as shown in Figs. 5a and b. These results clearly reveal that the electrophoretic deposit surface present an excellent super hydrophobicity due to the developed hierarchical surface structure. It is worthwhile to note that the electrophoretic deposition on the steel surface does not add further degradation on the steel surface. Therefore, this approach is promising to prepare a hydrophobic surface for large scale steel structures. This would be an extremely important advantage for the mass application of the hydrophobic processing in industrial applications.
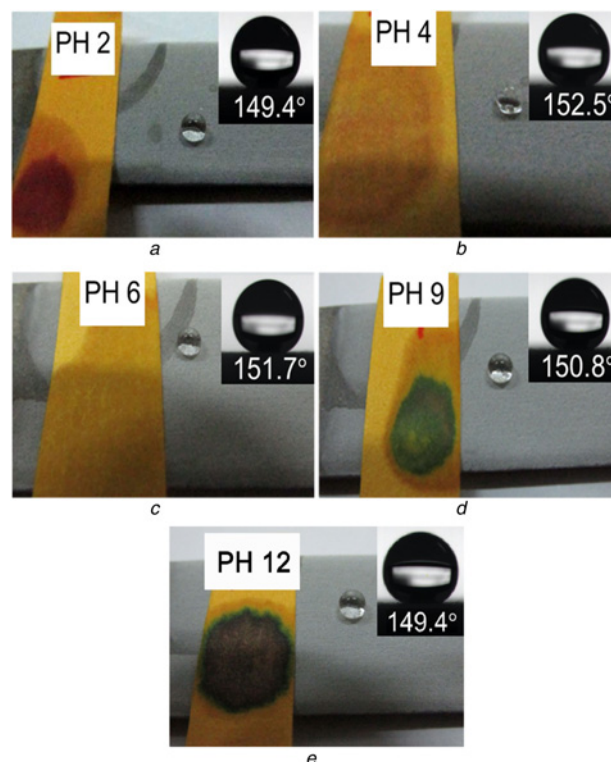

Fig. 5 *SAs of submicrometer Al_2O_3 surface by electrophoretic deposition on*
a Polished stainless steel
b Abrasive blasted stainless steel

Fig. 6 *CAs of the water droplets with different pH values of*
a 2
b 4
c 6
d 9
e 12 on the fabricated submicrometer Al_2O_3 on the blasted stainless steel. The yellow colour papers are pH indicator strips

3.2. Natural environment adaptability of the electrophoretic deposit surfaces: It is well known that the natural rain water is not always in a neutral condition of pH 7.0. Quantitative statistic studies show that the pH value of the natural rain generally varies in a wide range of <4.5 to >7.5 with a variety of factors [27]. To examine whether the super-hydrophobic surface prepared by the electrophoretic deposition of aluminium oxide performs effective super hydrophobicity in the natural environment, the CAs of water droplets with different pH values of 2, 4, 6, 9 and 12 on the fabricated submicrometer Al_2O_3 surfaces were examined and shown in Figs. 6a–e. The stable hydrophobicity with different pH values was also reported in the literature [28–31]. The results in our study indicate that the water droplets with different pH values cannot wet the submicrometer Al_2O_3 coated polished steel surface and the CAs can remain at ca. 150° for the water droplets with pH values of 4–9. The test results prove that the submicrometer Al_2O_3 surface by electrophoretic deposition on the metal substrates has an excellent adaptability to the natural environment. Therefore, the electrophoretic deposition of the submicrometer Al_2O_3 can be considered to be a promising approach which can be utilised widely in preparing super-hydrophobic engineering surfaces.

4. Conclusions: In summary, we have successfully fabricated a ceramic hierarchical structure on a metal (i.e. steel) surface through a facile and scalable electrophoretic deposition approach. Through the electrophoretic deposition of submicrometer alumina powders, followed by the modification with stearic acid as low surface energy material, the hierarchical alumina surface exhibits excellent super hydrophobicity with a CA of ca. 150° and a very low SA of ca. 3°. Meanwhile, the water droplets of pH 2 and 12 on the developed hierarchical surface remain a CA of ca. 150° while the water droplets with pH values of 4–9 remain a higher contact angel (i.e. >150°), indicating that the hierarchical alumina surface can maintain very good super-hydrophobic property particularly in a relatively natural environment (i.e. pH values in a range of 4–9). Due to the non-destructive effect on the substrate surface comparing with conventional abrasive blasting, the electrophoretic deposition of alumina can be regarded as a non-destructive approach for the steel structures. We believe that the developed approach combining the electrophoretic deposition of alumina and the modification with stearic acid would be favourable for the natural environment adaptive super-hydrophobic surface manufacture.

6 References

[1] Lee K., Lyu S., Lee S., *ET AL.*: 'Characteristics and self-cleaning effect of the transparent super hydrophobic film having nanofibers array structures', *Appl. Surf. Sci.*, 2010, **256**, pp. 6729–6735

[2] Kim T., Tahk D., Lee H.: 'Wettability-controllable super water- and moderately oil repellent surface fabricated by wet chemical etching', *Langmuir*, 2009, **25**, pp. 6576–6579

[3] Bhushan B., Jung Y., Koch K.: 'Self-cleaning efficiency of artificial superhydrophobic surfaces', *Langmuir*, 2009, **25**, pp. 3240–3248

[4] Li X., Reinhoudt D., Crego-Calama M.: 'What do we need for a superhydrophobic surface? A review on the recent progress in the preparation of superhydrophobic surfaces', *Chem. Soc. Rev.*, 2007, **36**, pp. 1350–1368

[5] Roach P., Shirtcliffe N., Newton M.: 'Progress in superhydrophobic surface development', *Soft Matter.*, 2008, **4**, pp. 224–240

[6] Zhang X., Shi F., Niu J., *ET AL.*: 'Superhydrophobic surfaces: from structural control to functional application', *J. Mater. Chem.*, 2008, **18**, pp. 621–633

[7] Ganesh V., Raut H., Nair A., *ET AL.*: 'A review on self-cleaning coatings', *J. Mater. Chem.*, 2011, **21**, pp. 16304–16322

[8] Hancock M., Sekeroglu K., Demirel M.: 'Bioinspired directional surfaces for adhesion, wetting, and transport', *Adv. Funct. Mater.*, 2012, **22**, pp. 2223–2234

[9] Liu X., Liang Y., Zhou F., *ET AL.*: 'Extreme wettability and tunable adhesion: biomimicking beyond nature?', *Soft Matter.*, 2012, **8**, pp. 2070–2086

[10] Gao X., Yan X., Yao X., *ET AL.*: 'The dry-style antifogging properties of mosquito compound eyes and artificial analogues prepared by soft lithography', *Adv. Mater.*, 2007, **19**, pp. 2213–2217

[11] Cao L., Jones A., Sikka V., *ET AL.*: 'Anti-icing superhydrophobic coatings', *Langmuir*, 2009, **25**, pp. 12444–12448

[12] Choi C., Kim C.: 'Large slip of aqueous liquid flow over a nanoengineered superhydrophobic surface', *Phys. Rev. Lett.*, 2006, **96**, pp. 066001-1–4

[13] Lee C., Choi C., Kim C.: 'Structured surfaces for a giant liquid slip', *Phys. Rev. Lett.*, 2008, **101**, pp. 064501-1–4

[14] Saito H., Takai K., Yamauchi G.: 'Water- and ice-repellent coatings', *Surf. Coat. Int.*, 1997, **80**, pp. 168–171

[15] Kulinich S., Farzaneh M.: 'Ice adhesion on super-hydrophobic surfaces', *Appl. Surf. Sci.*, 2009, **255**, pp. 8153–8157

[16] Blossey R.: 'Self-cleaning surfaces-virtual realities', *Nat. Mater.*, 2003, **2**, pp. 301–306

[17] Lafuma A., Quéré D.: 'Superhydrophobic states', *Nat. Mater.*, 2003, **2**, pp. 457–460

[18] Feng L., Li S., Li Y., *ET AL.*: 'Super-hydrophobic surfaces: from natural to artificial', *Adv. Mater.*, 2002, **14**, pp. 1857–1860

[19] Min W., Jiang B., Jiang P.: 'Bioinspired self-cleaning antireflection coatings', *Adv. Mater.*, 2008, **20**, pp. 3914–3918

[20] Hong X., Gao X., Jiang L.: 'Application of superhydrophobic surface with high adhesive force in no lost transport of superparamagnetic microdroplet', *J. Am. Chem. Soc.*, 2007, **129**, pp. 1478–1479

[21] Cho H., Kim D., Lee C., *ET AL.*: 'A simple fabrication method for mechanically robust superhydrophobic surface by hierarchical aluminum hydroxide structures', *Curr. Appl. Phys.*, 2013, **13**, pp. 762–767

[22] Wang G., Zhang T.: 'Oxygen adsorption induced superhydrophilic-to-superhydrophobic transition on hierarchical nanostructured CuO surface', *J. Coll. Interface Sci.*, 2012, **377**, pp. 438–441

[23] Joung Y., Buie C.: 'Antiwetting fabric produced by a combination of layer-by-layer assembly and electrophoretic deposition of hydrophobic nanoparticles', *ACS Appl. Mater. Interfaces*, 2015, **7**, pp. 20100–20110

[24] Darmanin T., Givenchy E., Amigoni S., *ET AL.*: 'Superhydrophobic surfaces by electrochemical processes', *Adv. Mater.*, 2013, **25**, pp. 1378–1394

[25] Lau C., Vuong T., Wang J., *ET AL.*: 'Hydrophobic to superhydrophobic surface modification using impacting particulate sprays', *Appl. Surf. Sci.*, 2014, **311**, pp. 89–94

[26] Yu S., Wang X., Wang W., *ET AL.*: 'A new method for preparing bionic multi scale superhydrophobic functional surface on X70 pipeline steel', *Appl. Surf. Sci.*, 2013, **271**, pp. 149–155

[27] Charlson R., Rodhe H.: 'Factors controlling the acidity of natural rainwater', *Nature*, 1982, **295**, pp. 683–685

[28] Xi J., Feng L., Jiang L.: 'A general approach for fabrication of superhydrophobic and superamphiphobic surfaces', *Appl. Phys. Lett.*, 2008, **92**, pp. 053102-1–4

[29] Zhang E., Wang Y., Lv T., *ET AL.*: 'Bio-inspired design of hierarchical PDMS microstructures with tunable adhesive superhydrophobicity', *Nanoscale*, 2015, **7**, pp. 6151–6158

[30] Yokoi N., Manabe K., Tenjimbayashi M., *ET AL.*: 'Optically transparent superhydrophobic surfaces with enhanced mechanical abrasion resistance enabled by mesh structure', *ACS Appl. Mater. Interfaces*, 2015, **7**, pp. 4809–4816

[31] Wang N., Yuan Y., Wu Y., *ET AL.*: 'Wetting transition of the caterpillar-like superhydrophobic Cu/Ni-Co hierarchical structure by heat treatment', *Langmuir*, 2015, **31**, pp. 10807–10812