VERSITA

Cent. Eur. J. Chem. • 10(6) • 2012 • 1766-1772
DOI: 10.2478/s11532-012-0116-0

Central European Journal of **Chemistry**

Fabrication of superhydrophobic surface of stearic acid grafted zinc by using an aqueous plasma etching technique

Short Communication

Jinzhang Gao*, Yaping Li, Yan Li,
Hongwei Liu, Wu Yang

Chemistry & Chemical Engineering College,
Northwest Normal University, Lanzhou 730070, P. R. China

Received 22 April 2012; Accepted 17 June 2012

Abstract: A stable superhydrophobic surface of stearic acid grafted zinc was fabricated with two steps, that is, the zinc surface was firstly treated with glow discharge electrolysis plasma (GDEP) and then followed by a grafted reaction of stearic acid onto the treated zinc surface. Results indicated that the wettability of zinc substrate changed from superhydrophily to superhyphodrobicity with a water contact angle (CA) up to 158° and a water sliding angle (SA) less than 5°. The surface morphology and composition were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively.

Keywords: *Superhydrophobic surface • Zinc substrate • Glow discharge electrolysis plasma (GDEP)*

© Versita Sp. z o.o.

1. Introduction

Study on the superhydrophobic surfaces of solid materials has attracted many scientists to move their focus to this area due to its importance in industry [1-8]. In general, a surface with a water contact angle (CA) more than 150° and a sliding angle (SA) less than 10° is considered to be a super-hydrophobic surface. According to the Cassie-Baxter equation [9], both rough surface and low surface free energy material are prerequisite for a high contact angle, thus, most attempts to fabricate superhydrophobic surfaces fall into the two categories [10]. One centers around methods that enlarge the roughness of materials' surface [11-14], the other one involves lower materials' surface free energy [7,15-20]. For a smooth surface, the CA increases only up to 120° around, therefore building a suitable micro-structure is the key for preparation a superhydrophobic surface. At present, it has been developed a number of methods to construct surface micro-structure, such as chemical etching [11], electrospinning [12], electrodeposition [13], hydrothermal [14], and so on. So far, very few papers [22] reported the application of glow discharge electrolysis technique in this field.

Glow-discharge electrolysis is a non-Faradaic electrochemical process, which occurs at solution surface or under aqueous solution as the applied voltage over a critical value. Since there are many energetic species in the glow-discharge area like plasma, it is called the glow-discharge electrolysis plasma (GDEP) [21]. GDEP can be considered as a green technique in synthetic chemistry, environmental science and surface treatment. During GDEP, many active species such as ·OH, ·H and H_2O_2 are produced with yields much higher than those expected on the basis of faraday's law. These energetic species can be used to alter the surface of materials chemically or physically [22,23], for instance, it can rough the surface or endow the surface with special chemical functionalities. Thereby, plasma treatment is a useful tool in the modification of surface, and one promising result from plasma treatments is that the surface hydrophilicity can be improved dramatically [24]. In the present paper, the glow-discharge electrolysis plasma (GDEP), which has been focused on the modification of polymer, was

---

* *E-mail: jzgao@nwnu.edu.cn*

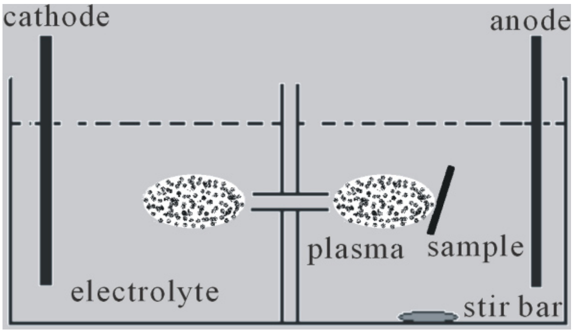

Figure 1. GDEP setup.

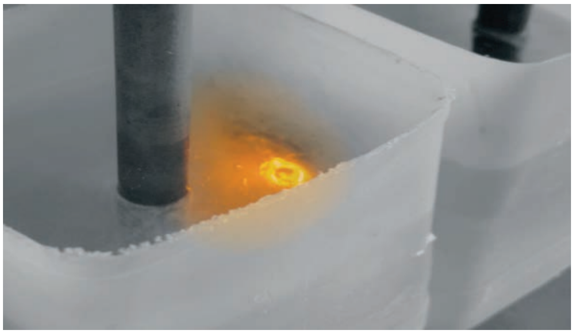

Figure 2. Photo of GDEP.

used for the first time to pretreat zinc surface to fabricate superhydrophobic surface of stearic acid grafted zinc in aqueous solution.

2. Experimental procedure

2.1. Glow discharge electrolysis plasma

The experimental apparatus consists of a high voltage power supply unit and a reactor (Fig. 1). The Model LW100J2DC power supply provided a voltage of 0 ~ 1000 V and a current in a range of 0 ~ 1 A. The reactor is composed of two electrodes submerged in an electrochemical cell separated by a dielectric wall with a diaphragm. The volume of the reactor's internal cell was 800 mL, with the graphite-discharged electrode. The assembly together with the capillary is manufactured from quartz glass in order to avoid contaminations on the prepared materials' surface. For obtaining the better glow discharge, a few of diluted Na_2SO_4 solutions were used as supporting electrolytes. Fig. 2 is a real photo of GDEP, where the reactor was coated by a water jacket, maintained at 298±2 K.

2.2. Fabrication of superhydrophobic zinc

A cleaned zinc sheet with purity of 99.99% (successively washed ultrasonically with acetone and ethanol for 10 min) was placed in the GDEP reactor to etching and functionalize. During the pretreatment procedure, all parameters that affect the etching and functionalization on the zinc substrate, such as the concentration of supporting electrolyte, discharge voltage and discharge time, were examined in details, the hydrophilicity of zinc surface was taken as a reference. Then, the disposed zinc substrate was immersed in 0.05 M stearic acid ethanolic solution at 25°C for about 12 or 24 h *via* GDEP. Finally, superhydrophobic films were formed on the zinc substrate. The resulting product was thoroughly washed with absolute ethyl alcohol and distilled water to eliminate physical adsorption, and then dried at room temperature. Fig. 3 is a scheme of the formation process of superhydrophobic surface on zinc substrate.

2.3. Characterization

The scanning electron micrographs (SEMs) of zinc substrate were obtained with a field emission scanning electron microscope (JEOL JSM-6701F) at a voltage of 15.0 kV. The sample surfaces were gold-coated before analysis. The crystal structure of the substance on zinc substrate obtained was characterized using X-ray diffraction (XRD, Japan Science, D/MAX-2400). The composition of superhydrophobic films was analyzed by Fourier transform infrared spectrophotometer (FT-IR, US, FTS3000). The wettability was characterized by the measurement of water CA on its surface, using a commercial contact angle meter (CA-A, Shanghai, SL200B). The water CA was measured at five different points of each sample.

3. Results and discussion

3.1. Optimization of the etching conditions

3.1.1. Effect of concentration of the supporting electrolyte on hydrophilicity of zinc surface

In the study, Na_2SO_4 was used as an inert supporting electrolyte so that there was no remarkable change in conductivity during the whole electrolysis process. That is to say, the initial conductivity of the solution was just based on the concentration of Na_2SO_4 used in the electrolytic solution. The effect of concentration of the supporting electrolyte on hydrophilicity of zinc surface was studied from 0.5 to 10 g L^{-1}, and the results are showed in Fig. 4. It was noted that, each concentration studied above can make the zinc surface hydrophilic, with the water CA changing from initial 52° to about 15°. It was also observed that the extent from 4 g L^{-1} to 6 g L^{-1} may be more superior, which can cause the zinc surface superhydrophilic with water CA less than 10°. This is attributed to the fact that the initial

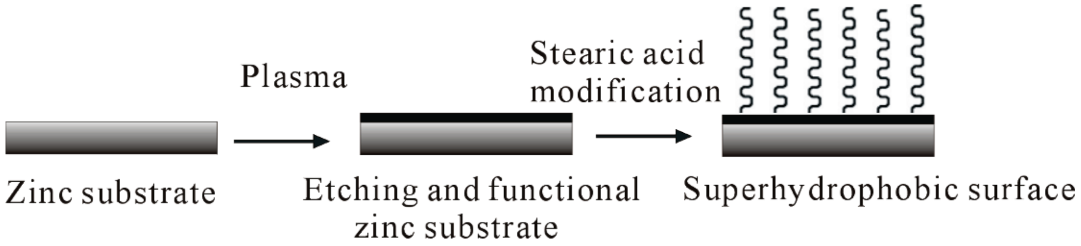

Figure 3. Scheme of the formation process for superhydrophobic surface on zinc substrate.

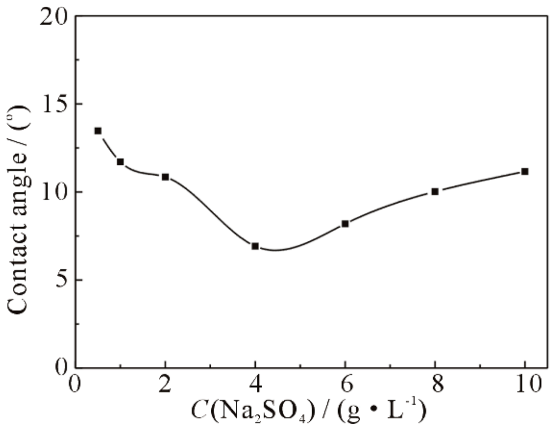

Figure 4. Effect of concentration of supporting electrolyte.

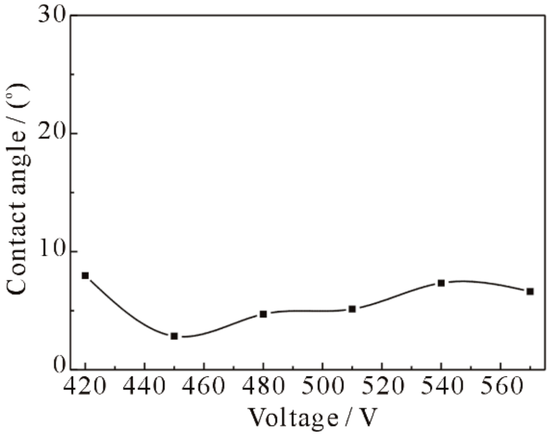

Figure 5. Effect of discharge voltage.

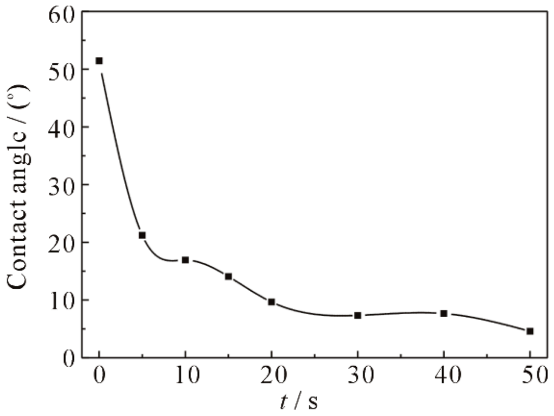

Figure 6. Effect of discharge time.

conductivity of the solution has a significant impact on the production of ·OH [21], as the Na_2SO_4 is a strong electrolyte, and the conductivity increased with increasing of its concentration. However, after the concentration increased to a certain extent, it would decrease, due to the interaction between positive and negative ions increases, reducing the rate of migration of ions.

3.1.2. Effects of discharge voltage and discharge time on hydrophilicity of zinc surface

In general, the amount of the free radicals generated by GDEP is relative to the discharge voltage and discharge time. In this paper, the effect of the discharge voltage on hydrophilicity of zinc surface from 420 to 570 V was examined. Moreover, there is no observable change in Fig. 5. Comparatively, the better range would be from 450 to 510 V. Perhaps, at the lower discharge voltage there is little of free radicals present, causing hardly a chemical reaction. With increasing the discharge voltage, the amount of free radical increases, a well hydrophilic micro-structure may be effectively formed. Moreover, the too high discharge voltage can also destroy the formed zinc substrate surface and the graphite anode. To obtain better results, the discharge time should be extended to more than 20 s at least (see Fig. 6), and the shorter discharge time is not enough to complete the etching process for the insufficient amount of free radicals.

3.2. Zinc surface morphology and composition after GDEP

Because the surface wettability is determined by the chemical components and surface roughness of solids, the formation of hierarchical structures is a key factor for the preparation of superhydrophobic surfaces. For example, the water CA for a smooth surface can only reach as high as 120°; for a micropatterned surfaces or a surface with hierarchical structures, it can reach more than 175° and even 180°. In this study, the pretreated zinc substrate has typical hierarchical structures (see Fig. 7). Fig. 7a shows the scanning electron microscopy (SEM) images of the morphology of structure obtained after GDEP pretreated, forming a dense filmlike layer. The high magnification image in Fig. 7b indicates that

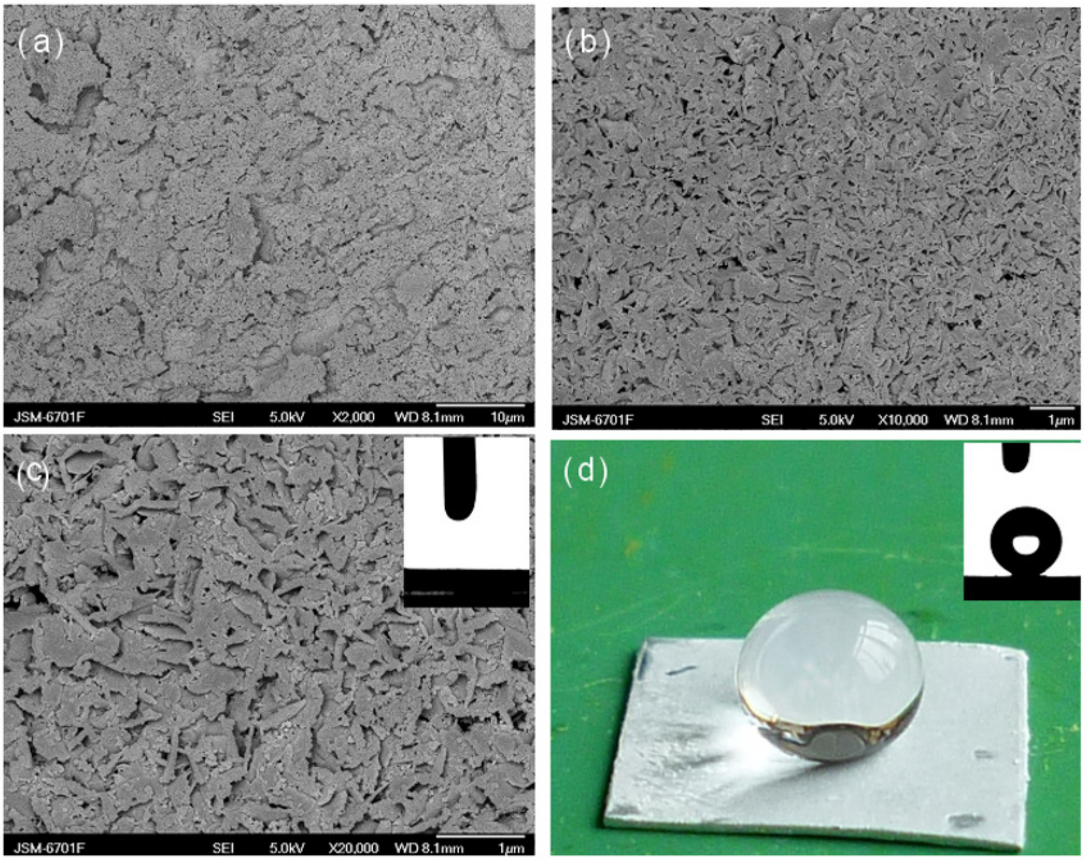

Figure 7. The SEM images of superhydrophilic surfaces constructed on zinc substrate by the GDEP process (a), (b), (c); (d) Digital photograph of 12 uL water droplet on superphydrophobic surface.

the film is composed by the compact leaflike cluster with about 500 nm long. Interestingly, Fig. 7c appears the abundant papillary particles on the leaflike clusters. Such roughed structures can trap air into the interstices of the micro- and nanotextured surfaces to increase the water CA. It happens because of the appropriate roughness on zinc substrate, which show superhydrophilic property with a water CA closing to 0^o (Fig. 7c CA image), due to the more roughness of surface, the better of hydrophilic to substance is. The micro- and nanostructures of zinc substrate surface provides a crucial condition to fabricate superphydrophobic surface. Indeed, the zinc substrate surfaces after stearic acid modified show strong hydrophobic, with the water CAs higher than 155° and the SAs are less than 5^o (Fig. 7d). Fig. 7d shows 12 *u*L of water droplets on the superhydrophobic surface shape, it does not penetrate into the groves, but is suspended on the rough surfaces. The water droplet is very unstable, when the surface is slightly tilted, the water droplets roll out quickly; if water droplets from the air drop down and impact the superhydrophobic surface, the phenomenon of bouncing back and forth occurs. Theory Cassie can explain this phenomenon. When the water droplets contact with the superhydrophobic surface, they cannot penetrate inside since the rough surfaces captured a lot of air, hence, the water droplets contact with a surface recombined of air and liner low surface energy materials. According to Cassie equation [25],

$$\cos\theta^* = f_s(1+\cos\theta_e) - 1, \quad (1)$$

Where f_s is the air fraction of the liquid-solid contact to the projected surface area (corresponding, $1-f_s$ is the air fraction of the liquid-air contact to the projected surface area). Here θ^* and θ_e are the contact angles on the rough surface composed of leaflike clusters and that on a smooth surface modified with the same coating, *i.e.*, $CH_3(CH_2)_{16}COOH$. Taking the θ_e as 100^o, the f_s value of the superhydrophobic surface with a water contact angle of 158^o is calculated to be 15%, that is to say, when water droplets contact with this surface, only about 15% of the interface is water droplets in contact with solid, and the other 85% of the area is water droplets in contact with air, which results in the super hydrophobic phenomenon. The results mentioned above could be easily understood

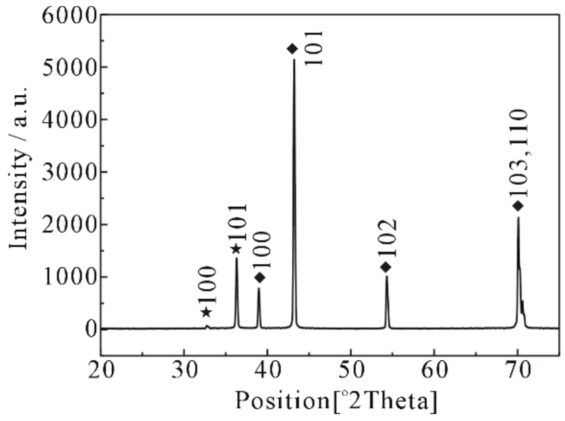

Figure 8. The XRD pattern of zinc substrate after GDEP treatment ((★)ZnO;(◆)Zn).

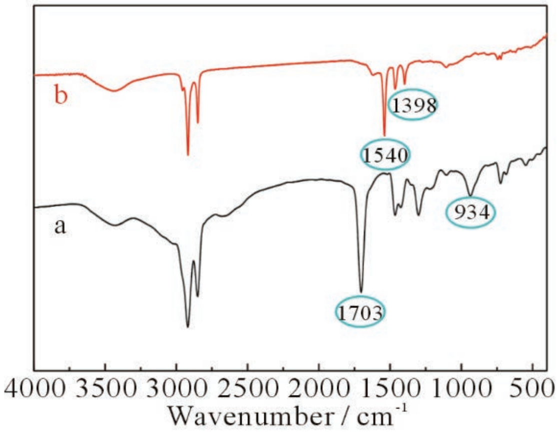

Figure 9. FT-IR spectra of stearic acid (a) and powders scraped from the superhydrophobic zinc surface (b).

by the following factors: The hierarchical structure reduced the contact area between solid and water at their interface to cause a higher water CA, and also reduced further the continuity of the three-phase contact line at the solid-liquid interface that induces a low sliding angle. Thereby, the micro- and nanostructures can not only improve the hydrophobicity, but also weaken the CA hysteresis, which is very important to self-cleaning properties of surfaces.

Furthermore, typical x-ray diffraction (XRD) patterns of the ZnO films fabricated on zinc substrate after treatment with GDEP are shown in Fig. 8. As shown in Fig. 8, in the small angle region a set of well-defined diffraction peaks is observed, in addition to the diffraction peaks from the zinc substrate, there is only one very strong (101) diffraction peak from zinc oxide, consisting with the surface color change from silver to white, whereas other zinc oxide peaks are either relatively weak or not detected. Thus, we conclude that the obtained surface has a composition of zinc oxide, *i.e.*, zinc can be rapidly oxidized after pretreatment with GDEP.

3.3. Infrared spectra analysis of superhydrophobic films

The chemical composition of superhydrophobic film is analyzed by Fourier transform infrared spectrophotometer (FTIR), after the stearic acid modification. FTIR analysis (see Fig. 9) indicates that the free -COOH band from stearic acid at 1703 cm^{-1} disappears, a group of new bands appears at 1539 and 1398 cm^{-1}, corresponding to the stearate characteristic absorption peaks, while, -OH bending vibration at 934 cm^{-1} is also greatly reduced. Thus, we conclude that the obtained surface has a composition of $Zn[CH_3(CH_2)_{16}COO]_2$.

In GDEP modification system, the chemically active species ·OH and H_2O_2 would play an important role in zinc substrate modification due to the strong oxidizing effect. Within an appropriate voltage, GDEP is created around a pointed anode in the aqueous solution, various chemically active species, such as H·, ·OH and H_2O_2, are formed in the solution due to bombardment of energetic H_2O^{+*} ions from the plasma.

$$H_2O^{+*} + nH_2O \longrightarrow n\,H{\cdot} + n\,{\cdot}OH + H_2O^{+}$$

$${\cdot}OH + {\cdot}OH \longrightarrow H_2O_2$$

In this study, as an environmental friendly and advanced electrochemical oxidation technology, GDEP technology leads the zinc substrate surface to formation of the zinc oxide film in a very short time, which can shorten the later reaction time of zinc and stearic acid, and the water CA can up to 155° within 12 hours fascinatingly.

Based on the change of the XRD, FTIR analysis of the experimental data and GDEP discussed above, the following chemical reaction equations for the formation of superhydrophobic films on the zinc substrate is suggested:

$$Zn \xrightarrow{GDEP} ZnO$$

$$ZnO + 2CH_3(CH_2)_{16}COOH \xrightarrow{RT} Zn[CH_3(CH_2)_{16}COO]_2$$

3.4. Wettability results

After 3 days of direct stearic acid modification, the cleaned and smooth zinc substrate (successively washed ultrasonically with acetone and ethanol for 10 min) changed hydrophobicity, with the water CA changing from 52° to 100°. However, the water CA on zinc surface, which was firstly treated with glow discharge electrolysis plasma (GDEP), and then followed by a grafted reaction of stearic acid onto the treated zinc surface, can reach up to 158° (see Fig. 7d).

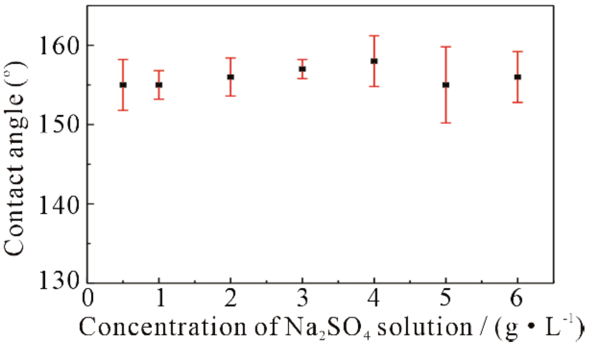

Figure 10. The relationship between concentration of Na_2SO_4 solution and the water CA on superphydrophobic surface.

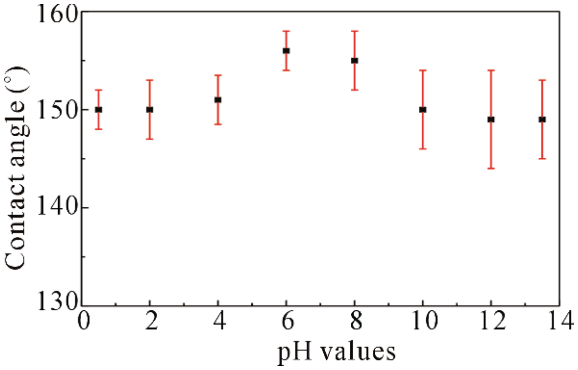

Figure 11. The relationship between pH values and the water CA on superphydrophobic surface.

From what have been discussed above, we can safely draw a conclusion that in addition to the modification of low surface energy materials, the establishment of an appropriate surface roughness is also an important factor in super-hydrophobic surface fabrication.

The stability of the superhydrophobic zinc surface obtained was also investigated. The water CA on the surface still maintains larger than 155° after storage in air for various time intervals (5 days, 10 days,1 month, 2 months, 4 months, 6 months), showing the long-term stability. In addition, the obtained surfaces show superhydrophobicity not just for distilled water but also for corrosive liquids concluding acidic, basic, and some aqueous salt solutions. Fig. 10 show the relationship between solutions of Na_2SO_4 in different concentrations and CAs on the superhydrophobic surface. It is noted that the obtained surface shows high CAs for the solutions of Na_2SO_4 in different concentrations, there is no obvious fluctuation of the water CAs on the superhydrophobic zinc surface within experimental error tailoring the concentration from 0.5 to 6 g L^{-1}, keeping a CA value larger than 150°. Furthermore, the droplets of the Na_2SO_4 solution can roll off easily from the surfaces, which reveals that the droplets do not permeate into the $Zn[CH_3(CH_2)_{16}COO]_2$ surface inhibiting the contact between metals and salt solutions. Moreover, it is noted that the fabricated surfaces show superhydrophobicity in the pH range from 0.5 to 13 (see Fig. 11). It is clear that there is no obvious fluctuation of the water CAs on the fabricated surface within experimental error tailoring at all pH values, keeping a constant value of about 150°, showing no effect of acid and base on the wettability of the surface. The protection of metal material from corrosion is an important project in modern society. The construction of superhydrophobic surfaces is one of the mostly used techniques. The above result is a good example.

4. Conclusions

In this study, glow discharge electrolysis plasma (GDEP) as a green technique has been used to fabricate a superhydrophobic surface on zinc substrate. The results showed that the GDEP treatment can change the morphology and crystallinity of zinc substrate surface, while amount of the O-containing functional groups on zinc sample increases. Various pretreatment parameters including concentration of supporting electrolyte, discharge current and pretreatment time, played significant roles on zinc substrate modification. On this basis, we modified the rough surfaces with low surface free energy material to fabricate the stable superhydrophobic film on zinc substrate, the presence of O-containing functional groups on zinc substrate accelerates the reaction between stearic acid and zinc substrate for the CA reaching to 155° in 12 hours. The prepared surfaces show superhydrophobicities even for corrosive liquids and have broad industry applications. This study provides a new method in construction of microstructures with unique surface wettabilities and it is likely that other metal materials may be similarly prepared by this technically feasible, highly efficient and cost effective attractive pretreatment method.

Acknowledgements

This work was supported in part by the Key Project of Science and Technology of Education Ministry (00250), the Natural Science Foundation of Gansu Province (3ZS041-A25-028; 096RJZA120), and the Project of KJCXGC-01 of Northwest Normal University, China.

References

[1] J.M. Xi, F. Lin, L. Jiang, Appl. Phys. Lett. 92, 053102 (2008)

[2] Z.G. Guo, W.M. Liu, B.L. Su, Appl. Phys. Lett. 92, 063104 (2008)

[3] M. Li, J. Zhai, H. Liu, Y.L. Song, L. Jiang, D.B. Zhu, J. Phys. Chem. B 107, 9954 (2003)

[4] X. Hong, X.F. Gao, L. Jiang, J. Am. Chem. Soc. 129, 1478 (2007)

[5] G.X. Li, B. Wang, Y. Liu, T. Tan, X.M. Song, H. Yan, Appl. Surf. Sci. 255, 3112 (2008)

[6] C.S. Liu, Z.W. Li, L. Wang, Z. Xu, Key Eng. Mater. 368, 1374 (2008)

[7] K.K.S. Lau, J. Bico, K.B.K. Teo, M. Chhowalla, G.A.J. Amaratunga, W.I. Milne, G.H. McKinley, K.K. Gleason, Nano Let. 3, 1701 (2003)

[8] W. C. Wu, M. Chen, S. Liang, X.L. Wang, J.M. Chen, F. Zhou, J. Colloid Interface Sc. 326, 478 (2008)

[9] E. Bormashenko, Colloids Surf. A 324, 47(2008)

[10] L. Feng, S. Li, Y.Li, H. Li, L. Zhang, J. Zhai, Y. Song, B. Liu, L. Jiang, D. Zhu, AdV. Mater. 14, 1857 (2002)

[11] B.T. Qian , Z.Q. Shen, Langmuir 21, 9007 (2005)

[12] M.L. Ma, Y. Mao, M. Gupta, K.K. Gleason, G.C. Rutledge, Macromolecules 38, 9742 (2005)

[13] X. Zhang, F. Shi, X. Yu, H. Liu, Y. Fu, Z.Q. Wang, L. Jiang, X.Y. Li, J. Am. Chem. Soc. 126, 3064 (2004)

[14] F. Shi, X.X. Chen, L.Y. Wang, J. Niu, J.H. Yu, Z.Q. Wang, X. Zhang, Chem. Mater. 17, 6177 (2005)

[15] B. Xu, Z.S. Cai, Appl. Surf. Sci. 254, 5899 (2008)

[16] J.P. Youngblood, T.J. McCarthy, Macromolecules 32, 6800 (1999)

[17] L. Zhai, F.Ç. Cebeci, R.E. Cohen, M.F. Rubner, Nano Lett. 4, 1349 (2004)

[18] X.Y. Ling, I.Y. Phang, G.J. Vancso, J. Huskens, D.N. Reinhoudt, Langmuir 25, 3260 (2009)

[19] T. Nishino, M. Meguro, K. Nakamae, M. Matsushita, Y. Ueda, Langmuir 15, 4321 (1999)

[20] H. Yabu, M. Takebayashi, M.Tanaka, M. Shimomura, Langmuir 21, 3235 (2005)

[21] J.Z. Gao, A.X. Wang, Y. Fu, J.L. Wu, D.P. Ma, X. Guo, Y. Li, W. Yang, Plasma Sci. Technol. 10, 30 (2008)

[22] R. Joshi, R.D. Schulze, A.M. Plath, J.F. Friedrich, Plasma Proc. Polym. 5, 695 (2008)

[23] M.B.O. Riekerink, J.G.A. Terlingen, G.H.M. Engbers, J. Feijen, Langmuir 15, 4847 (1999)

[24] D.S. Wavhal, E.R. Fisher, Langmuir 19, 79 (2003)

[25] A.B.D. Cassie, S. Baxter, Trans. Faraday Soc. 40, 546 (1944)