JOURNAL OF Applied Polymer SCIENCE

Patterned Polymer Surfaces with Wetting Contrast Prepared by Polydopamine Modification

Liang Zhang,[1,2] Haizhu Yu,[1] Ning Zhao,[2] Zhi-Min Dang,[1] Jian Xu[2]
[1]Department of Polymer Science and Engineering, School of Chemistry and Biological Engineering, University of Science & Technology Beijing, 100083, People's Republic of China
[2]Beijing National Laboratory for Molecular Sciences, Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China
Correspondence to: Z.-M. Dang (E-mail: dangzm@ustb.edu.cn) and J. Xu (E-mail: jxu@iccas.ac.cn)

ABSTRACT: Patterned polymer surfaces with contrasting wettability are prepared by polydopamine (PD) modification. The fabrication process involves spraying dopamine solution droplets on hydrophobic polymer surfaces and PD deposition derived from the oxidative polymerization of dopamine. Each dopamine solution droplets functions as microreactor leading to the formation of patterned PD thin films on the solid/liquid interfaces. Multiple kinds of polymer substrates, including polypropylene, polystyrene, polycarbonate, polyethylene and polytetrafluoroethylene, are endowed with PD patterns using this method. Two types of wetting behaviors are achieved in relation to the micro morphology of the substrates. If smooth or porous substrates are used, the as-formed film exhibited hydrophilic-hydrophobic pattern. When a hierarchical-structured film is used, the uncoated and coated regions have similar static wettability but different dynamic wetting behavior. This PD modification method is also proved to be suitable for flexible and curved surfaces. The results along with the fact that PD could deposit on virtually any surfaces makes this method find wide practical applications in many fields. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41057.

KEYWORDS: coatings; films; morphology; surfaces and interfaces

Received 27 March 2014; accepted 21 May 2014
DOI: 10.1002/app.41057

INTRODUCTION

Surface wettability is an essential characteristic of solid surface in many biological processes and industrial applications. Patterning solid surfaces with wetting contrast has received increasing attention due to its potential applications in the development of functional materials and various devices. Wetting contrast patterning could be used for water collection founded in naturally occurring surfaces. For instance, Namib Desert Stenocara beetles use alternating hydrophilic bumps and superhydrophobic channels on the back to collect drinking water from fog-laden wind.[1] The difference in wettability between hydrophilic and hydrophobic regions can be used for patterning water-soluble or water-dispersed materials, including inorganic salt,[2,3] nanoparticles,[4,5] proteins,[6] and cells.[7–9] Hydrophilic-hydrophobic patterning also plays a vital role in "printed electronics," since the hydrophilic region in a hydrophobic substrate helps define the functional inks to achieve sufficient resolution.[10] Recently, Levkin et al.[11] presented a way of transferring micropatterns in porous polymer films onto adhesive tapes and used the replicated patterns for reverse cell transfection. Hwang's group[12] fabricated different wettability in different surface areas using laser radiation. It could design complex patterns to distort water droplets in shape and bulges. Surface patterning has also been realized by other methods, such as dewetting,[13] lithography,[14] vapor deposition,[15] and microcontact printing.[16,17] However, many of the techniques are time-consuming and laborious, and cannot satisfy the need to achieve low cost production of large scale patterning. In addition, the reported works usually focused on static wetting contrast, patterns with dynamic wetting contrast were seldom addressed.

Inspired by the exceptional adhesive performance of mussels, a new versatile and universal surface modification method has recently been established by employing an *in-situ* oxidative polymerization of dopamine at alkaline pH.[18–21] Dopamine is considered as a structure mimic of 3,4-dihydroxy-L-phenylalanine (DOPA) found in the mussel adhesive protein, which could polymerize into polydopamine (PD) and form a thin coating

Additional Supporting Information may be found in the online version of this article.

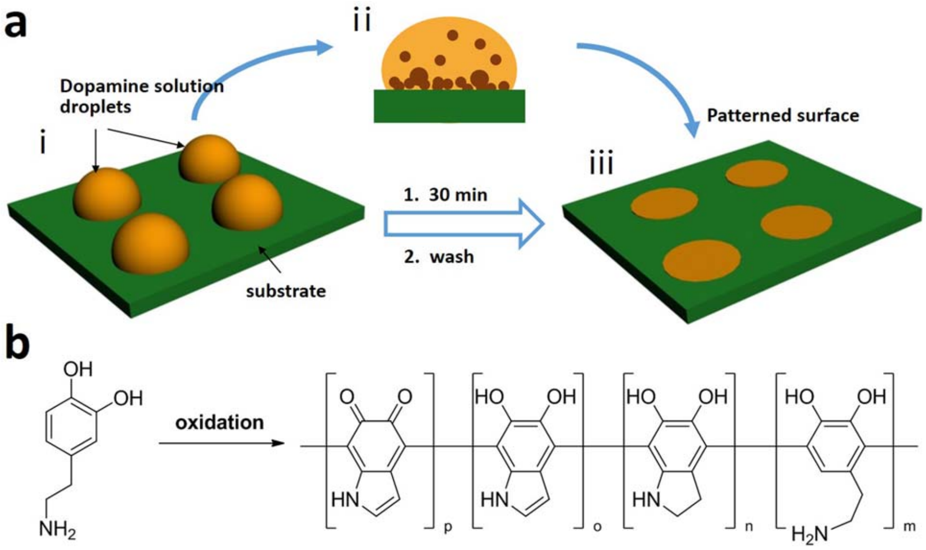

Figure 1. (a) Schematic illustration of the preparation procedure of hydrophilic-hydrophobic patterned surface by PD deposition. (b) Possible PD structure from oxidative polymerization of dopamine. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

onto surfaces. The PD coating not only can be deposited on virtually all kinds of materials, including silica, ceramics, metals, oxides, and polymers, but also can act as an impactful platform because it is capable to be functionalized through reactions with amino- or mercapto-nucleophiles. These remarkable properties allow it to find a wide range of applications in nanotechnology,[22–24] electrical,[25–27] and biological fields.[28–30] In this work, by taking advantage of the hydrophilic nature of PD coating, we developed a simple and rapid route to a variety of patterned surfaces with contrasting wettability. Dopamine solution was sprayed onto hydrophobic surfaces to form numbers of droplets. The droplets performed as micro-reactors, generating PD thin coatings at the interface of the solid/liquid contacting area to provide the hydrophilic region. A series of polymer substrates with different micromorphology were investigated, including polypropylene (PP), polytetrafluoroethylene (PTFE), polyethylene (PE), polystyrene (PS), and polycarbonate (PC). Not only hydrophilic-hydrophobic patterned surfaces were fabricated, but also patterns with similar static wettability yet opposing dynamic wet behaviors were demonstrated. This method was also found to be suitable on flexible and curved surfaces.

EXPERIMENTAL

Tris(hydroxymethyl) aminomethane (Beijing Chemical Company, AP), dopamine hydrochloride (Sigma, AP), HCl, acetone, ethanol (Beijing Chemical Works, CP) and deionized water were used as received. PP, PE, and PTFE membranes were bought commercial products and were washed by ethanol and deionized water before use. Hierarchically structured PC film was prepared according to a literature.[31] Generally, the surface of PC film was coated with acetone and then immersed in water. After dried, the film obtained hierarchical structure.

Dopamine hydrochloride (2 mg/mL) was dissolved in 10 m*M* Tris-HCl solution and then the pH of the solution was adjusted to 8.5. The dopamine solution was sprayed on hydrophobic polymer surfaces. And then the substrate along with the droplets was carefully put into a homemade humidity box with relative humidity (RH) of 90%. After 30 min, the substrate was taken out and washed thoroughly. The sample was dried in room environment before characterization.

The morphology of the films was observed by field emission scanning electron microscopy (SEM, Hitachi S-4300), operating at 15 kV. X-ray photoelectron spectrometry (XPS) spectra were recorded on AXIS ULTRA DLD (A Shimadzu Group Company Kratos). The static water contact angles (CAs) of the surfaces were measured on Krüss Drop Shape Analysis System-100 (DSA 100) by a sessile water drop method with 3 μL water drops. Reported data are averages of 3 measurements at different places on the sample. Because the PD modified regions of the achieved patterned surface were too small for the sessile water drop method, CA of PD modified surfaces were measured using a counterpart prepared by the same process with 0.3 mL of dopamine droplets placed on the substrates instead of spray.

RESULTS AND DISCUSSION

The typical process of fabricating patterned surface assisted by PD deposition is shown in Figure 1(a). Dopamine solution was sprayed on a hydrophobic substrate to form numerous microdroplets. Every droplet worked as an individual microreactor with the same dopamine concentration and pH value. To prevent the droplets from evaporation, the microdroplets attached substrate was put in a box with humidity of 90 RH%. Otherwise, water would vaporize quickly at ambient environment due to the large surface area of the microdroplets, leaving the solute on the surface. The color of the dopamine solution droplets changed to brown in a few minutes and gradually turned darker. After 30 min, the substrate was taken out and washed. PD thin films were formed on the liquid/solid interface. As a result, a PD patterned surface was achieved.

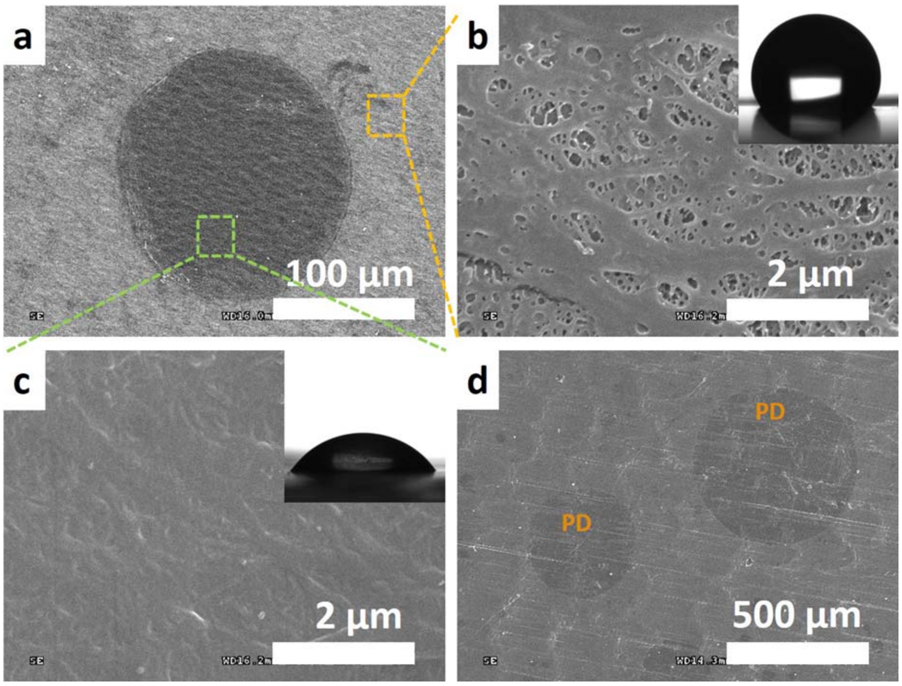

Figure 2. SEM images of (a) hydrophilic-hydrophobic patterned PP surface, (b) unmodified region of (a), (c) PD modified region of (a), and (d) hydrophilic-hydrophobic patterned PTFE surface. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The chemical structure of PD and its assembly mechanism that results in thin films are yet not clearly known. It was proposed that PD adopted linear structure which composed of dihydroxyindole, indoledione, and dopamine units [Figure 1(b)]. Dopamine was presumed to first form the indole skeleton by oxidative ring closure and the 5,6-dihydroxyindole monomers were covalently cross-linked via aryl–aryl linkages on different possible reaction sites on the indole ring.[21,32–34] Lee et al. identified that both noncovalent self-assembly and covalent polymerization contributed to the formation of PD.[35] In the dopamine solution droplets, the polymerization took place at the substrate/liquid surface forming PD layer; simultaneously in the solution, the monomer units composed of several 5,6-dihydroxyindole molecules were likely to assemble into nanoaggregates, which were capable of linking to each other forming PD particles.[36] The nanoaggregates and relatively small-sized PD particles in the solution could incorporate into the deposited PD layer contributing to the formation of thin films. But large PD particles with tens to hundreds of nanometers could not participate in the deposition and were collected when the microdroplets were washed (Supporting Information Figure S1).

A hydrophilic-hydrophobic patterned PP film was fabricated using the PD modification method. PD thin film was proved to be formed on the PP surface by XPS analysis (Supporting Information Figure S2). SEM image of the patterned surface is shown in Figure 2(a). The dark region represents the PD modified area, which exhibited circular shape as an imprint of the contacting area of dopamine solution droplet and substrate. Compared with uncoated part, the pristine PP surface which showed microporous structures [Figure 2(b)], the PD coated region was rather smooth with no apparent porous structure, although minor fluctuation can be seen due to the roughness of the PP membrane [Figure 2(c)].

The wettability of the film surfaces were characterized by water CA. It is known that surface wettability is governed by surface chemical composition and micro topology.[37] Surface roughness can enhance the wetting behavior of the solid, leading hydrophilic surface to more hydrophilic and hydrophobic surface to more hydrophobic. The CA of the pristine PP membrane was measured at 122.9 ± 1.4°, which originated from the porous structure and the hydrophobic capacity of PP film. After treated by dopamine solution, the water CA of the hydrophilic area turned to 65.2 ± 3.4°. This CA value was close to the theoretical value, 45–65°, of PD film.[21,38] The hydrophilicity of the PD modified region presented an obvious wetting contrast for the uncoated PP surface. This preparation procedure was repeated on a relatively smooth PTFE membrane. PTFE is commonly considered as an adhesion resistant material due to the low surface energy. Its extreme hydrophobicity makes it unable to be wetted by most kinds of liquids. Many efforts have been put to improve the hydrophilicity of PTFE. By using the PD deposition method, the SEM image shows PD was also well deposited on the PTFE surface after modification [Figure 2(d) and Supporting Information S3], similarly to the patterned PP surface. The PD thin coatings didn't come off even after ultrasonic treatment, which proved good adhesion. These results show that the PD modification method is effective and reliable for materials with extremely low surface energy.

An interesting difference in dynamic wetting was found by using the PD modification method on extremely rough substrates. A hierarchically structured PC film with water CA of 144.1 ± 1.4° was fabricated by solvent induced crystallization

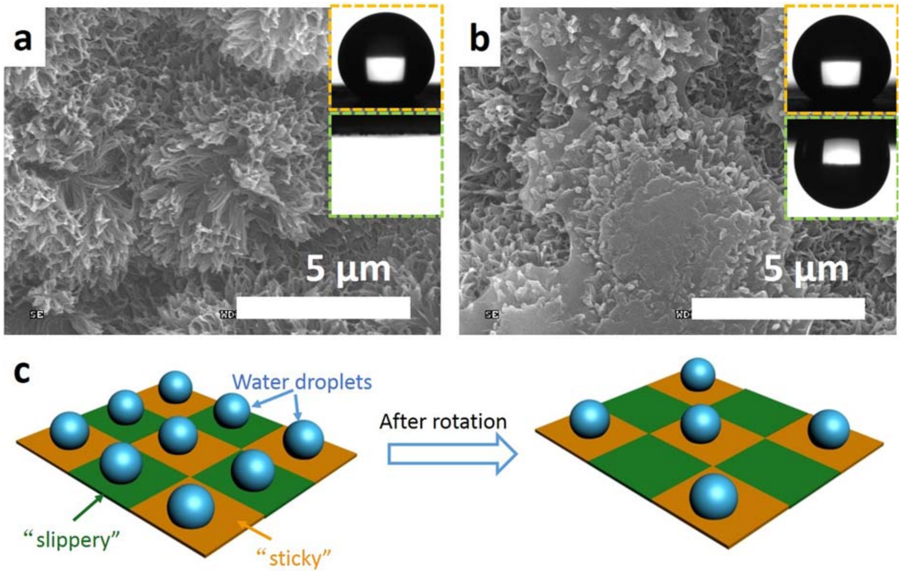

Figure 3. SEM images of (a) hierarchical-structured PC surface and (b) PD modified PC surface. Insets in (a) and (b) show a water droplet sitting on the corresponding surfaces and after the surfaces were turned upside down. (c) Illustrations of water droplets sitting on PD patterned rough surface. The uncoated regions show "slippery" hydrophobicity, which is easy for water droplets to roll off, whereas the coated regions display "sticky" hydrophobicity with droplet-adhesive ability. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

[Figure 3(a)]. After patterned with PD, the modified area on the PC surface still expressed hydrophobicity with a high CA of 142.9 ± 1.7°, which showed not much decrease compared with before. However, the dynamic wetting behavior of the two regions displayed large diversity. The uncoated region showed "slippery" hydrophobicity with water sliding angle of 10.2 ± 2.0°, which meant water droplets could easily roll off; whereas the PD modified region possessed "sticky" hydrophobicity because water droplets could be captured on the surface and hanged onto the surface even if it was upside down [Figure 3(b)]. This special wetting behavior was the result of the interplay of the microstructure and surface component. The SEM image shows that the coated region was not entirely covered by PD. It was rather a discontinuous film with some PC nanorods sticking out. The formation of this particular morphology could be ascribed to the highly hydrophobic property of the PC film. The hierarchical rough structure of PC film was capable of capturing a large amount of air in the nanostructures. During the

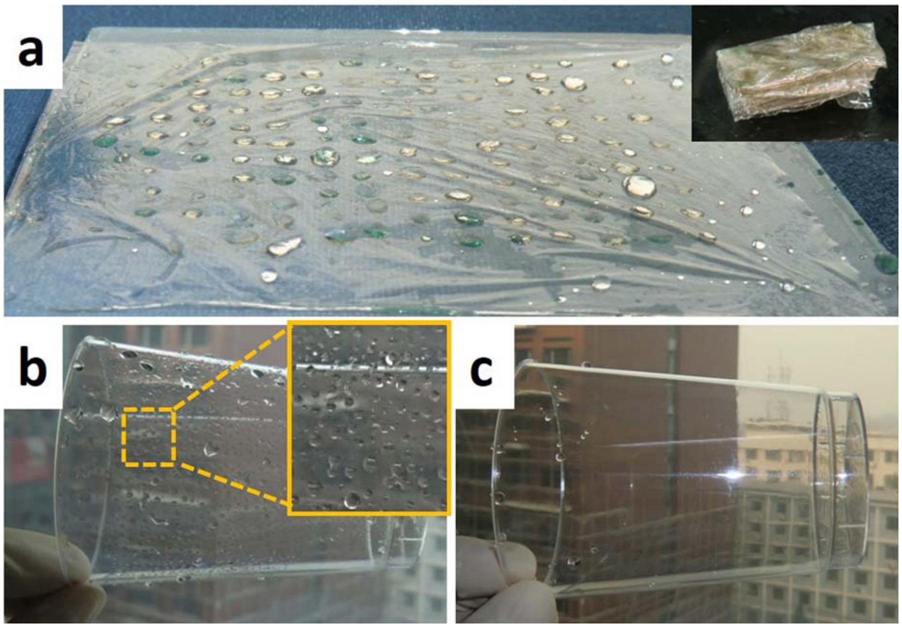

Figure 4. Photograph of (a) hydrophobic-hydrophilic patterned PE surface with water droplets arrays after folding and unfolding for 10 cycles. Inset of (a) is the patterned PE film in folding. (b) Hydrophobic-hydrophilic patterned and (c) untreated PS cup after flushed by water. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

modification process, the trapped air worked as air cushions holding the dopamine solution droplets up. As a result, the dopamine solution could not wet into the nanostructures but was only in contact with the top of the rough structures. And PD layers were deposited only at the solid/liquid contacting area. The rough microstructure and the uncovered PC nanorods led to the high CA of the surface, while the PD layers ensured the adhesion of the water droplets. Consequently, a "sticky"-"slippery" patterned surface with high water CAs was achieved [Figure 3(c)]. These findings demonstrated that the microstructure of the substrate had a large impact on the achieved wetting behaviors of the PD modified surfaces.

The PD modification method was also tested on flexible and curved surfaces. A large piece of PE membrane and a PS cup underwent the typical PD modification procedure. To achieve a better view, the hydrophilic-hydrophobic pattern was enlarged by micro-pipetting dopamine solution droplets on a hydrophobic PE membrane with the size of 11 × 11 cm^2. The diameter of each PD domains was about 3 mm. The as-achieved membrane preserved flexibility after the treatment. The film could be folded for many times as shown in Figure 4(a). After folding and unfolding for ten cycles, no signs of damage of the PD coatings were seen. The film was immersed in water and dragged out, water droplet arrays based on the PD patterns were presented on the film, indicating the wettability was not jeopardized by the folding [Figure 4(a)]. A PS cup was treated by spraying the dopamine solution on the external surface. PD thin films were deposited along the curve of the cup appearing light brown color. After flushed by water, the as-formed surface could capture micro water droplets on the hydrophilic domains, indicating the PD layers were successfully deposited on the surface [Figure 4(b)]. In comparison, without modification, the PS cup was too hydrophobic to seize any water droplets by flushing under water [Figure 4(c)]. These results show that this method have no difficulty in performing on curving surfaces and may also be used on irregular surface shapes. This versatile method can be used on large scales and make potential applications in water collection and liquid control.

CONCLUSIONS

A PD modification method of fabricating patterned surface with contrasting wettability was demonstrated. Microdroplets of dopamine solution were used as microreactors to form PD thin films at the solid/liquid contacting area. The hydrophilic property of PD thin films provided large wetting contrast to the hydrophobic substrates. Multiple types of hydrophobic polymer were endowed with hydrophilic patterns. Hydrophilic-hydrophobic patterned surfaces were achieved on smooth and porous substrates, whereas "sticky"-"slippery" patterns with high CAs were attained on hierarchical-structured substrate. This method was proved to be suitable for curved and flexible surfaces. The as-formed patterned surfaces could find wide applications in water collection, fluidic control and liquid immobilization. In addition, because PD could be a platform as secondary reactions, the patterned surfaces could be used as a foundation for further exploitation in biology and electric fields.

ACKNOWLEDGMENTS

This work was supported by NSFC (No. 51303010), China Postdoctoral Science Foundation (No. 2013M540047), Specialized Research Fund for the Doctoral Program of Higher Education (20130006120019), and the Fundamental Research Funds for the Central Universities (No. FRF-TP-13–024A).

REFERENCES

1. Parker, A. R.; Lawrence, C.R. *Nature* **2001**, *6859*, 33.
2. Aizenberg, J.; Black, A. J.; Whitesides, G. M. *Nature* **1999**, *398*, 495.
3. Qin, D.; Xia, Y. N.; Xu, B.; Yang, H.; Zhu, C.; Whitesides, G. M. *Adv. Mater.* **1999**, *11*, 1433.
4. Zhong, Z. Y.; Gates, B.; Xia, Y. N.; Qin, D. *Langmuir* **2000**, *16*, 10369.
5. Liu, S. H.; Tok, J. B. H.; Locklin, J.; Bao, Z. N. *Small* **2006**, *2*, 1448.
6. Piret, G.; Coffinier, Y.; Roux, C.; Melnyk, O.; Boukherroub, R. *Langmuir* **2008**, *5*, 1670.
7. Notsu, H.; Kubo, W.; Shitanda, I.; Tatsuma, T. *J. Mater. Chem.* **2005**, *15*, 1523.
8. Komori, K.; Nada, J.; Nishikawa, M.; Notsu, H.; Tatsuma, T.; Sakai, Y. *Anal. Chim. Acta* **2009**, *2*, 222.
9. Ishizaki, T.; Saito, N.; Takai, O. *Langmuir* **2010**, *11*, 8147.
10. Sirringhaus, H.; Kawase, T.; Friend, R. H.; Shimoda, T.; Inbasekaran, M.; Wu, W.; Woo, E. P, *Science* **2000**, *290*, 2123.
11. Auad, P.; Ueda, E.; Levkin, P. A. *Acs Appl. Mater. Inter.* **2013**, *5*, 8053.
12. Lee, C.; Cho, H. D.; Kim, D.; Hwang, W. B. *Appl. Surf. Sci.* **2014**, *288*, 619.
13. Thickett, S. C.; Neto, C.; Harris, A. T. *Adv. Mater.* **2011**, *32*, 3718.
14. Jeyaprakash, J. D.; Samuel, S.; Rühe, J. *Langmuir* **2004**, *23*, 10080.
15. Gau, H.; Herminghaus, S.; Lenz, P.; Lipowsky, R. *Science* **1999**, *5398*, 46.
16. Drelich, J.; Wilbur, J. L.; Miller, J. D.; Whitesides, G. M. *Langmuir* **1996**, *7*, 1913.
17. Pompe, T.; Fery, A.; Herminghaus, S.; Kriele, A.; Lorenz, H.; Kotthaus, J. P. *Langmuir* **1999**, *7*, 2398.
18. Waite, J. H.; Tanzer, M. L. *Science* **1981**, *212*, 1038.
19. Waite, J. H. *Int. J. Adhes. Adhes.* **1987**, *7*, 9.
20. Waite, J. H.; Qin, X. X. *Biochemistry* **2001**, *40*, 2887.
21. Lee, H.; Dellatore, S. M.; Miller, W. M.; Messersmith, P. B. *Science* **2007**, *318*, 426.
22. Kang, S. M.; Park, S.; Kim, D.; Park, S. Y.; Ruoffand, R. S.; Lee, H. *Adv. Funct. Mater.* **2011**, *21*, 108.
23. Guo, L. Q.; Liu, Q.; Li, G. L.; Shi, J. B.; Liu, J. Y.; Wang, T.; Jiang, G. B. *Nanoscale* **2012**, *4*, 5864.
24. Zhang, L.; Wu, J. J.; Wang, Y. X.; Long, Y. H.; Zhao, N.; Xu, J. *J. Am. Chem. Soc.* **2012**, *134*, 9879.

25. Liao, Y.; Cao, B.; Wang, W.C.; Zhang, L.Q.; Wu, D.Z.; Jin, R.G. *Appl. Surf. Sci.* **2009**, *255*, 8207.
26. Chen, S. G.; Chen, Y.; Lei, Y. H.; Yin, Y. S. *Electrochem. Commun.* **2009**, *11*, 1675.
27. Ryou, M. H.; Lee, D. J.; Lee, J. N.; Lee, Y. M.; Park, J. K.; Choi, J. W. *Adv. Energy Mater.* **2012**, *2*, 645.
28. Tao, C. H.; Yang, S. R.; Zhang, J. Y.; Wang, J. Q. *Appl. Surf. Sci.* **2009**, *256*, 294.
29. Zhou, H.; Liu, Y. F.; Chi, W. D.; Yu, C. Y.; Yu, Y. J. *Appl. Surf. Sci.* **2013**, *282*, 181.
30. Zhang, X. M.; Li, Z. Y.; Yuan, X. B.; Cui, Z. D.; Yang, X. J. *Appl. Surf. Sci.* **2013**, *284*, 732.
31. Zhao, N.; Weng, L. H.; Zhang, X. Y.; Xie, Q. D.; Zhang, X. L.; Xu J. *Chem. Phys. Chem.* **2006**, *7*, 824.
32. Arzillo, M.; Mangiapia, G.; Pezzella, A.; Heenan, R. K.; Radulescu, A.; Paduano, L.; d'Ischia, M. *Biomacromolecules* **2012**, *13*, 2379.
33. Liebscher, J.; Mrówczyński, R.; Scheidt, H. A.; Filip, C.; Hădade, N.D.; Turcu, R.; Bende, A.; Beck, S. *Langmuir* **2013**, *29*, 10539.
34. Lin, S. C.; Chen, C. T.; Bdikin, I.; Ball, V.; Gracio, J.; Buehler, M. *J. Soft Matter* **2014**, *10*, 457.
35. Hong, S.; Na, Y. S.; Choi, S.; Song, I. T.; Kim, W. Y.; Lee, H. *Adv. Funct. Mater.* **2012**, *22*, 4711.
36. Jiang, J. H.; Zhu, L. P.; Zhu, L. J.; Zhu, B. K.; Xu, Y. Y. *Langmuir* **2011**, *27*, 14180.
37. Wenzel, R. N. *Ind. Eng. Chem.* **1936**, *28*, 988.
38. Wei, Q.; Zhang, F. L.; Li, J.; Li, B. J.; Zhao C. S. *Polym. Chem.* **2010**, *9*, 1430.