

Study on the Formation of Superhydrophobic Biomimetic Coating upon Raw Corroded Steel Surface

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Superhydrophobic biomimetic coating was achieved upon raw corroded steel surfaces by chemical modification. The in-situ textures of steel surfaces with different corroded conditions were utilized as the microscale feature of the superhydrophobic biomimetic coating, and the hierarchical structures in the form of perpendicular flake-like nanostructure formed by chemical modification as the nanoscaled feature. The spectra of Fourier transform infrared-attenuated total reflectance showed the formed biomimetic coating was chemically bonded with the steel surface for all samples. The average contact angles for the superhydrophobic biomimetic coating on slightly, moderately and seriously corroded steel surfaces were 149°, 161° and 158°, respectively. This superhydrophobic biomimetic coating can be a basement of applying SH surface in the anticorrosion of pipelines in the future.

Keywords: Superhydrophobic biomimetic coating, Micro-nano structure, Corroded steel surface, Chemical modification, Anticorrosion

1. INTRODUCTION

Superhydrophobic (SH) surface [1-9], which was found in numerous plant surfaces and body parts of certain insects and animals [10-12], attract great attention in corrosion resistance [13], microfluidics [14], and many others [15-17]. Superhydrophobic surface usually comprises two factors, i.e. microscale feature and nanoscaled feature with low surface energy. A lotus leaf surface has a special micro-nano binary structure, consisting of an array of randomly distributed micropapillae with diameters ranging from 5µm to 10µm, and these micropapillae are covered with waxy hierarchical structures in the form of branch-like nanostructures with an average diameter of about 125nm [18]. In recent years, many SH surfaces have been prepared through various methods based on the hierarchical

structure of lotus leaf surface. Both Gao et al. [19] and Ke et al. [20] have fabricated SH surfaces by using SiO₂ micro- and/or nano- particles as microscale and nanoscale protrusions on glass substrates. Yuan et al. have prepared a novel honeycomb-like SH polydimethylsiloxane surface templated by hierarchical rose petal surfaces [21]. Vinayak et al. have reported hierarchical silica coatings on glass by a sol-gel route [22]. Yang et al. reported a functional silica film on stainless steel mesh with tunable wettability [23]. Yuan et al. reported a facile method to fabricate stable superhydrophobic polystyrene surface by adding ethanol [24]. Jin et al. have prepared superhydrophobic nanocellulose aerogel membranes [25]. And Boscher et al. studied the influence of cyclic organosilicon precursors on the corrosion of aluminium [26].

Gas transportation by metal pipelines usually encounters fatal corruptions of pipeline, resulting in great economic loss and bad social impact [27]. The corrosion matters, carbon dioxide, sulfur dioxide and water of gas erode metal pipeline severely. Corrosion resistant agent is commonly alternative for anticorrosion of metal surface. Commonly, wet corrosion matters erode oxide layer of metal at first, and then penetrate the oxide layer, ensuing further corrosion and producing more oxide. Given their strong water repulsive properties, SH surfaces upon the oxide layer are an ideal candidate for slowing the breakdown of the metal oxide layer and thereby slowing corrosion of the metal layer underneath for pipelines.

In this paper, in-situ formation superhydrophobic biomimetic coating on raw corroded steel surface is studied. The in-situ microscale texture of the corroded surfaces acted as the microscopical feature of the biomimetic structure, and a novel hierarchical surface feature with low surface energy formed from surface modification by chemical agents as the nanoscaled feature. This study can be a basement of applying SH surface in the anticorrosion of pipelines in the future.

The effects of surface roughness on the wettability of the SH biomimetic structure were studied by scanning electron microscope (SEM) and Fourier transform infrared-attenuated total reflectance (FTIR-ATR). The contact angles (CAs) of water for SH surfaces were measured by optical contact angle meter (OCA).

2. EXPERIMENTS

A. Chemical modification

Steel sheets (4cm×3cm×0.8cm) from in-service natural gas pipelines (the impurity of the natural gas mainly contains carbon dioxide and water) with slightly, moderately, and seriously corroded surfaces were utilized as the model samples. Methyl trimethoxy silane (MTMS) and n-dodecyl trimethoxy silane (DTMS) were used as the modifying agent, n-hexane and 95wt.% ethanol as the solvent. All chemicals used were of analytical grade and were used as received without any further purification. MTMS and DTMS were solved in mixed solvent of n-hexane and 95wt.% ethanol (the pH value of the solution was measured as 6). The mol ratio of MTMS to DTMS was 1:1. Before modification, all steel sheets were swept with high speed air flow (ranging from 5 to 10m/s), rinsed with deionized water, and dried by infrared fast dryer. Under stir condition, the corroded surfaces of

the pretreated steel sheets were immersed in the solution of MTMS and DTMS for 3h. Then the surface samples were washed with deionized water and naturally dried in a neat atmosphere. The process was repeated for three times.

B. Anticorrosion test

500ml volumetric flasks with 25ml 5% NaCl neutral solution were put in water-bath at 50°C. The volumetric flasks were full of gaseous corrosion matters. The raw steel surface samples and the steel surface samples with superhydrophobic biomimetic coating were put in the volumetric flasks with a distance of 25mm from the bottom of the flasks (other surfaces of all the steel sheets were sealed with solid wax). After 3 days, all the steel surface samples were gently rubbed using parchment paper and washed with rapid deionized water for 10 minutes to get rid of the corrosion products, and were dried in an infrared drier. The anticorrosion rate was calculated according to the weight loss of steel sheet samples before and after experiment.

C. Characterization

The effects of surface roughness and chemical composition on the wettability of the SH nano-film were studied by SEM (CamScan MX2600, England) and FTIR-ATR (Bruker Vector 22, Germany). Contact angles (CAs) of water for the SH surfaces were measured by OCA (Dataphysics OCA20, Germany).

3. RESULTS AND DISCUSSION

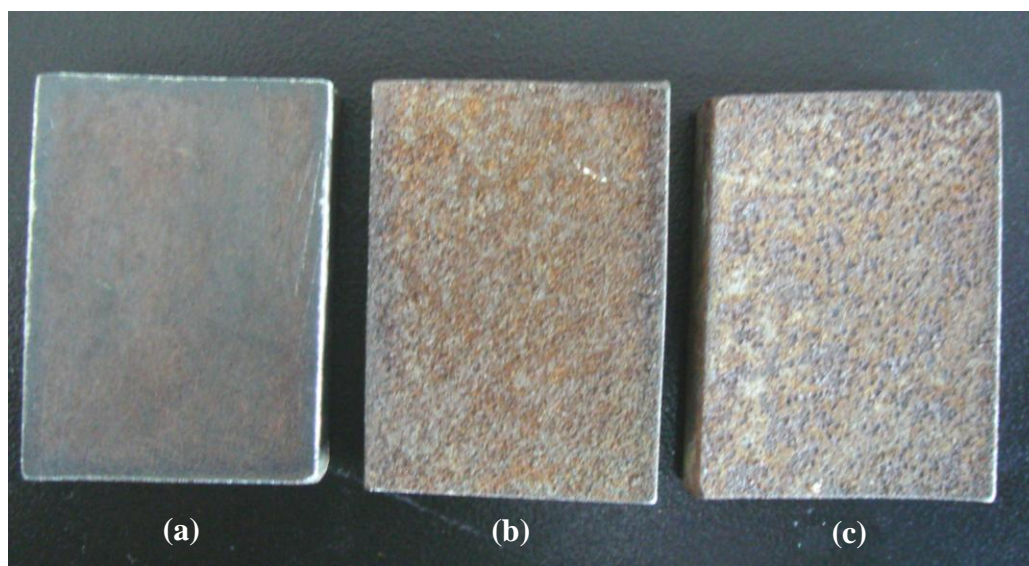


Figure 1. The pictures of steel sheets from in-service natural gas pipelines with (a) slightly, (b) moderately, and (c) seriously corroded surfaces

Figure 1 shows the pictures of steel sheets from in-service natural gas pipelines with slightly, moderately, and seriously corroded surfaces. Figure 2 shows the SEM micrographs of slightly, moderately and seriously corroded steel surfaces. The surface for all samples had rough microscaled morphologies.

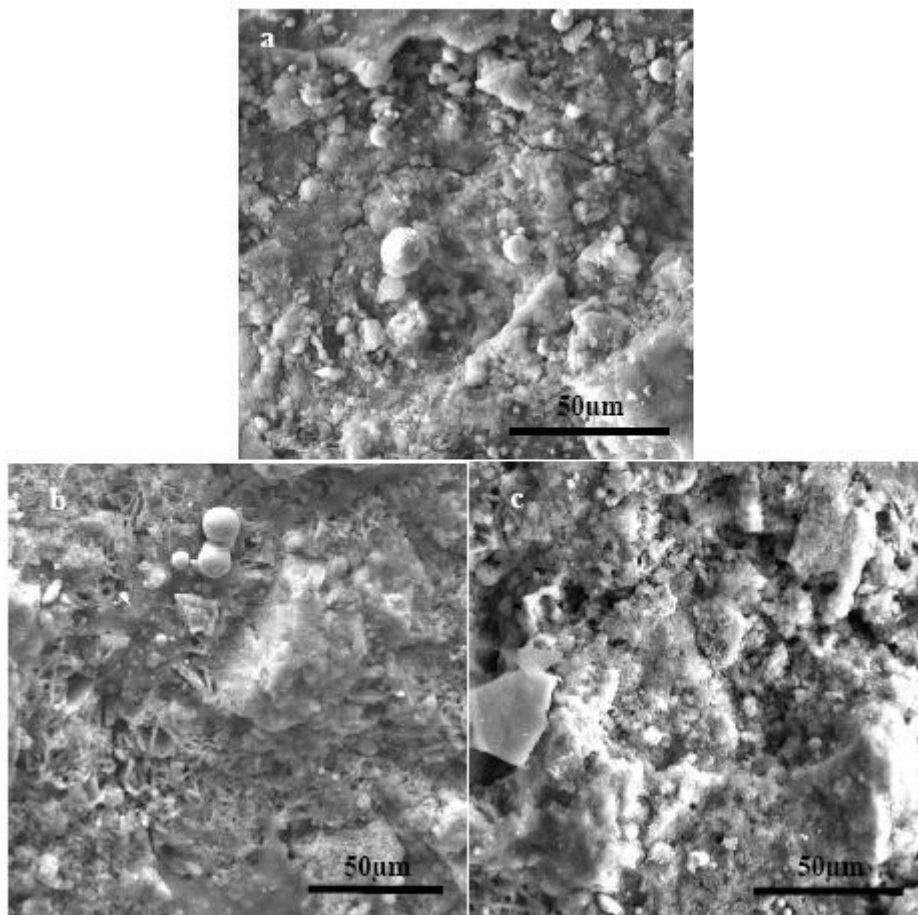


Figure 2. SEM micrographs of (a) slightly, (b) moderately and (c) seriously corroded steel surfaces

All the samples, especially the moderately corroded surface in Fig. 2b, had many randomly distributed protrusions with a size ranging from $5\mu\text{m}$ to $20\mu\text{m}$. These protrusions were the results of steel surface corrosion. It should be mentioned that similar rough microscaled morphologies were ubiquitous in other surface samples.

Figure 3 demonstrates the SEM micrographs and contact angles of slightly, moderately and seriously corroded steel surfaces after chemical modification. The steel surfaces had a layer of hierarchical structures in the form of perpendicular flake-like nanostructures after modification. For all the three samples, the perpendicular nano-flakes had a width ranging from 50nm to 200nm and a thickness of about 40nm , and for the moderately corroded surface sample, a very interesting fold-like morphology formed by uniform perpendicular nano-flakes was obtained. The thickness of the hierarchical structure layers was only several hundreds nanometers (See the arrow denoted of Fig. 3a, and the actual thickness was close to the highness of perpendicular nano-flakes). The combination of the in-situ protrusions of Fig. 2 and the hierarchical structures of Fig. 3 made the steel surfaces have superhydrophobic properties.

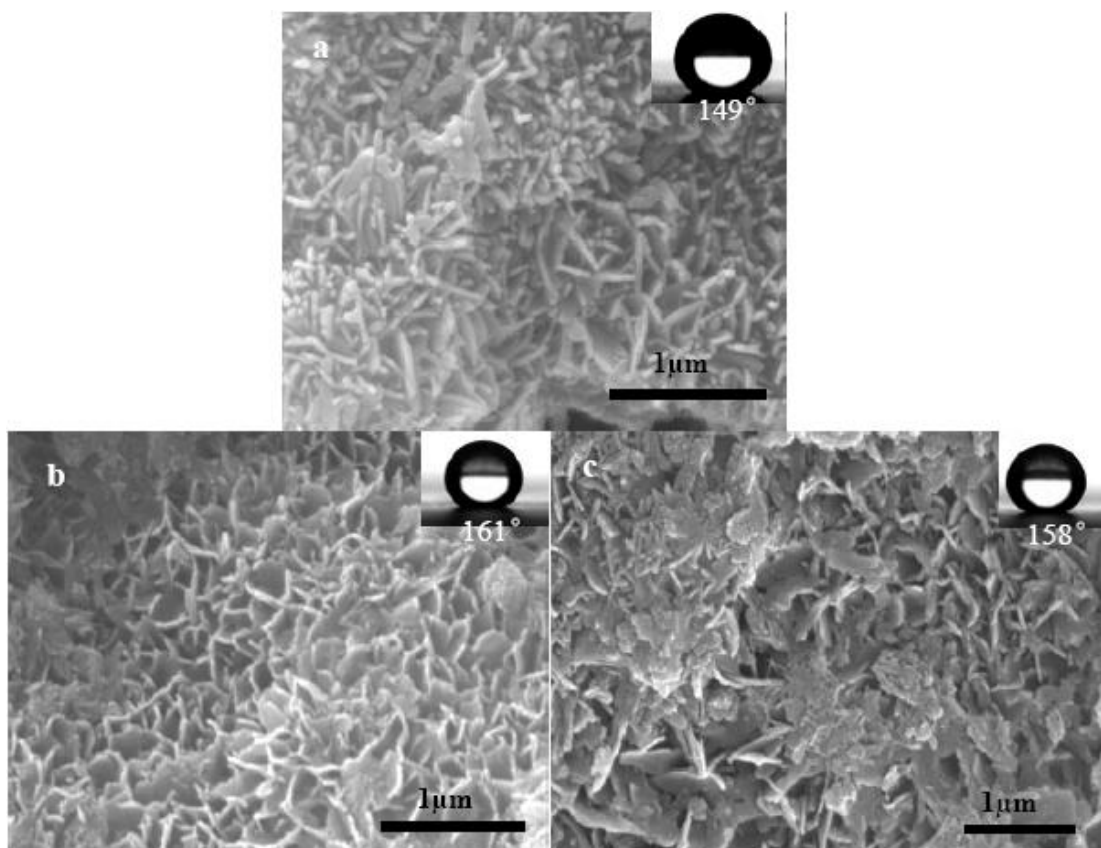


Figure 3. SEM micrographs and contact angles of (a) slightly, (b) moderately and (c) seriously corroded steel surfaces after chemical modification



Figure 4. The pictures of water drops on (a) raw and (b) chemical modified moderately corroded steel surfaces

After modification, the contact angles of the slightly, moderately and seriously corroded surfaces were $149 \pm 1^\circ$, $161 \pm 1^\circ$ and $158 \pm 1^\circ$, respectively (top right of Fig. 3). And the sliding angles of the three samples were about 4° , 3° and 3° , respectively. Figure 4 shows the pictures of water drops on raw and chemical modified moderately corroded steel surfaces. The water drops totally wetted the raw

moderately corroded steel surfaces. But for the chemical modified moderately corroded steel surfaces i.e. the superhydrophobic biomimetic coating steel surface, was little wetted.

Table 1. the properties of SH biomimetic layer upon slightly corroded steel surfaces before and after being corroded by 5wt.% NaCl aqueous solution for 3 days

Sample	M/g	M'/g	R/%	$\theta/ (^{\circ})$	$\theta'/ (^{\circ})$
1	85.1328	84.6745	78.42	70±1	—
1'	84.6493	84.5504		149±1	129±1
2	83.5125	82.9736	76.38	67±1	—
2'	85.1458	85.0161		152±1	134±1

Note: 1 and 2 were the samples before being eroded; 1' and 2' were the samples after being eroded. R was the anticorrosion rate; θ and θ' was the contact angle of the samples before and after being eroded, respectively. The same as Table 2 and Table 3.

Table 2. the properties of SH biomimetic layer upon moderately corroded steel surfaces before and after being corroded by 5wt.% NaCl aqueous solution for 3 days

Sample	M/g	M'/g	R/%	$\theta/ (^{\circ})$	$\theta'/ (^{\circ})$
1	87.8067	86.2461	89.93	66±1	—
1'	87.4626	87.4061		164±1	141±1
2	85.0251	84.5236	89.72	63±1	—
2'	84.9542	84.9026		161±1	139±1

Table 3. the properties of SH biomimetic layer upon seriously corroded steel surfaces before and after being corroded by 5wt.% NaCl aqueous solution for 3 days

Sample	M/g	M'/g	R/%	$\theta/ (^{\circ})$	$\theta'/ (^{\circ})$
1	82.2956	81.8598	85.46	57±1	—
1'	83.3548	83.2914		158±1	135±1
2	87.6617	87.0152	83.75	54±1	—
2'	87.7125	87.6074		159±1	137±1

The superhydrophobic biomimetic coatings had good anticorrosion property. The average anticorrosion rate of the SH moderately corroded surface in our experiments was about 89.8%, and the average anticorrosion rate of the SH slightly and seriously corroded surface was 77% and 84%, respectively (see Table 1, Table 2 and Table 3). The SH moderately corroded surface had the highest contact angle, therefore had the best anticorrosion property. The SH surfaces still had a high contact angle after being corroded by 5wt.% NaCl aqueous solution for 3 days, indicating these SH surfaces had a good stability.

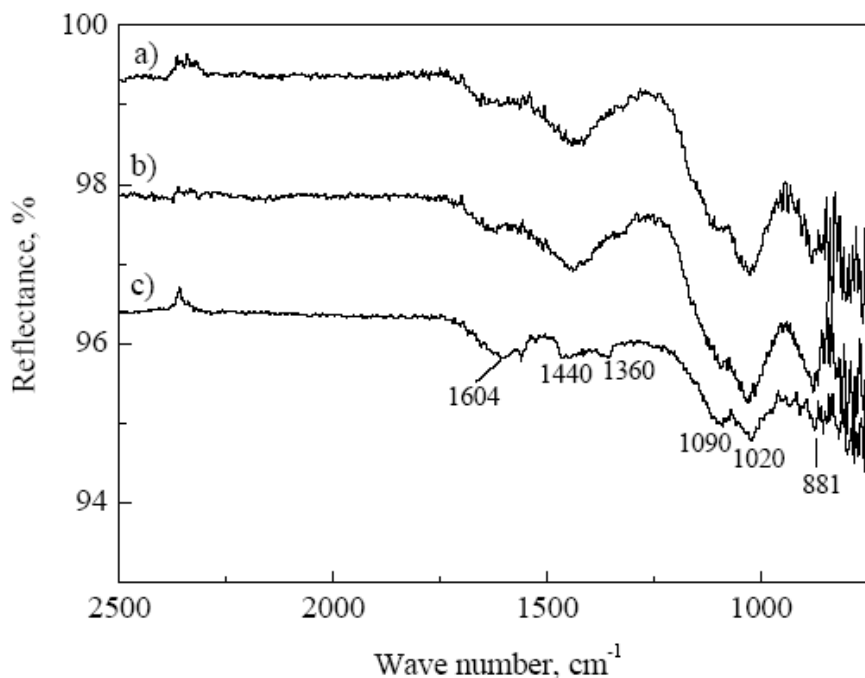


Figure 5. FTIR-ATR spectra of the corroded steel sheet surfaces: (a) slightly, (b) moderately and (c) seriously corroded surface

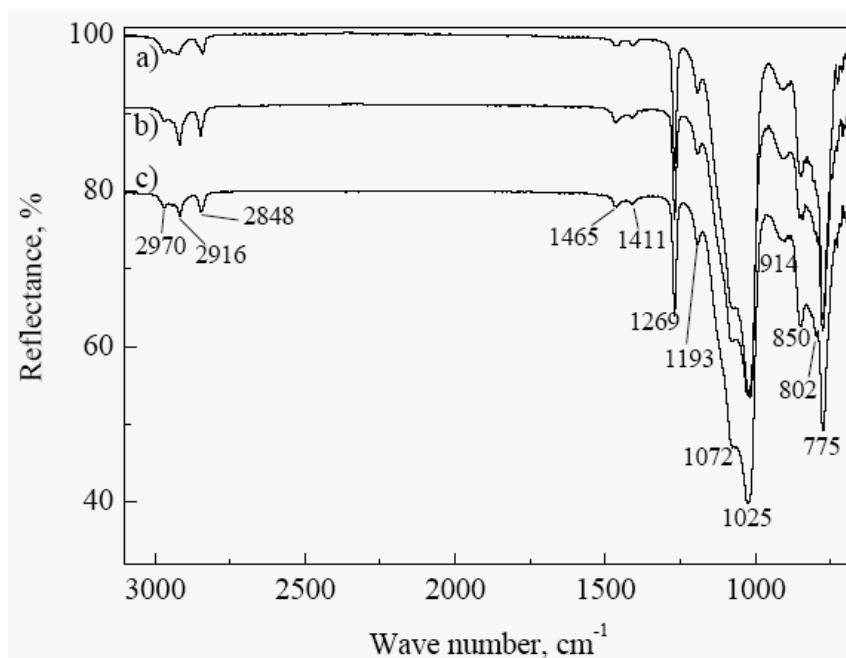


Figure 6. FTIR-ATR spectra of the corroded steel sheet surfaces after modification: (a) slightly, (b) moderately and (c) seriously corroded surface

Figure 5 gives the FTIR-ATR spectra of the unmodified steel sheet surfaces. The band at 893cm^{-1} and 1020cm^{-1} attribute to $\alpha\text{-FeOOH}$ and $\gamma\text{-FeOOH}$, respectively. The bands at 1084cm^{-1} and 1604cm^{-1} come from FeCO_3 . And the bands at 1440cm^{-1} and 1360cm^{-1} attribute to Fe_2O_3 . These results were in accordance with the real work condition of the in-service natural gas pipelines. The corrosion

mediums were mainly carbon dioxide and water. Therefore, the resulted corrosion layer of steel sheets was mainly composed of FeOOH , FeCO_3 and Fe_2O_3 . Figure 6 shows the FTIR-ATR spectra of the SH nano-film of the modified steel sheet surfaces. The band at 2970cm^{-1} attributed to $-\text{CH}_3$, the bands at 2916cm^{-1} and 2848cm^{-1} came from $-\text{CH}_2$. The peak at 1072cm^{-1} and 775cm^{-1} was respectively ascribed to dissymmetric flexing and symmetric flexing of Si-O-Si . The peak at 1465cm^{-1} came from $-\text{CH}_3$ asymmetry bending of alkyl chains. The peaks at 1411cm^{-1} and 1269cm^{-1} were the results of $-\text{CH}_3$ bending of $-\text{Si}(\text{CH}_3)_x$. The bands at 850cm^{-1} and 802cm^{-1} were ascribed to the stretching vibration of Si-C . These results indicated that the formed SH nano-film was chemically bonded with the steel surface.

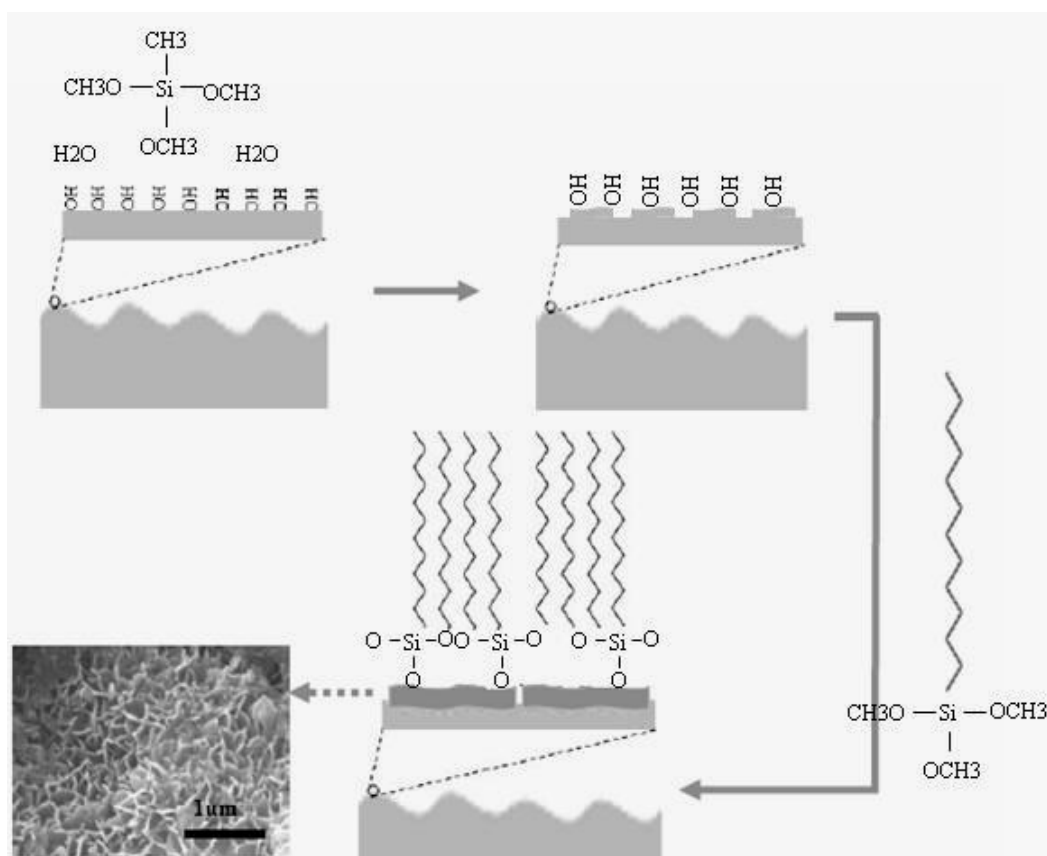


Figure 7. Schematic chart for formation process of superhydrophobic biomimetic coating upon corroded steel surface

In the formation process of the superhydrophobic biomimetic coating, the in-situ textured corrosion surfaces of corroded steel surfaces acted as rough factors and the chemical modification formed the nano-film with alkyl brushes of superhydrophobic surface through reacting with $-\text{OH}$ groups of steel surface, as shown in Fig. 7. In the solution, MTMS was hydrolyzed and reacted with $-\text{OH}$ groups of steel surface. Meanwhile, the hydrolyzed DTMS reacted with hydrolyzed MTMS, resulting in the formation of perpendicular nano-flakes with alkyl brushes on the surfaces.

Our data demonstrate that the formation of superhydrophobic biomimetic coating on raw steel surface can substantially enhance the protection of steel from corrosion. The application of the modified composition on raw steel surfaces renders the treated surfaces superhydrophobic with highly water-repellent property. Apparently, the alteration of steel surface changes the wetting mode of the surface from initially homogeneous (Wenzel model) to heterogeneous (Cassie-Baxter model) mode, where substantial amount of air is trapped in-between the water droplet and the substrate. The enhancement of the anticorrosion rate depends on the initial steel surface morphology. The randomly distributed protrusions with a size ranging from 5 μm to 20 μm acted as the micro-roughness and the perpendicular flake-like nanostructures from modifications as the nano-roughness. But the modified moderately and seriously corroded surfaces had more distributed protrusions caused by corrosion. Therefore the modified moderately and seriously corroded surfaces had better superhydrophobic nature and better anticorrosion property. While the modified slightly corroded surface had good superhydrophobic nature and anticorrosion property even lower than the moderately and seriously corroded ones did. This may be due to the formed perpendicular flake-like nanostructures are similar and the nano-roughness in the raw steel surface superhydrophobic biomimetic system is dominating.

The suggested modification of raw steel surface is simple, cost-effective and an efficient approach for the improved protection of steel pipelines from corrosion. The present coating technique can't solve the corrosion problems of in-service uncoated gas pipelines. This study makes the trenchless coating the inner surface of in-service gas pipelines with a superhydrophobic biomimetic coating possible.

4. CONCLUSION

The corrosion layer of the corroded steel sheets was mainly composed of FeOOH, FeCO₃ and Fe₂O₃. The modifying agent was chemically bonded with the steel surface. Superhydrophobic biomimetic coatings were successfully formed upon corroded steel surfaces with different corroded conditions. The formed biomimetic structure had hierarchical structures in the form of perpendicular flake-like nanostructures. The average contact angles of the superhydrophobic biomimetic coating on slightly, moderately and seriously corroded surfaces were 149°, 161° and 158°, respectively.

References

1. F. Xia and L. Jiang, *Adv. Mater.*, 20 (2008) 2842.
2. X. Zhang, F. Shi, J. Niu, Y.G. Jiang, and Z.Q. Wang, *J. Mater. Chem.*, 18 (2008) 621.
3. J. Genzer and A. Marmur, *MRS Bull.*, 33 (2008) 742.
4. M. Liu, Y. Zheng, J. Zhai, and L. Jiang, *Acc. Chem. Res.*, 43 (2010) 368.
5. D. Quéré, *Annu. Rev. Mater. Res.*, 38 (2008) 71.
6. J. W. M. Bush and D. L. Hu, *Annu. Rev. Fluid Mech.*, 38 (2006) 339.
7. F. Shi, J. Niu, J. Liu, F. Liu, Z. Wang, X.Q. Feng, and X. Zhang, *Adv. Mater.*, 19 (2007) 2257.
8. X. Q. Feng, X. F. Gao, Z. N. Wu, L. Jiang, Q. S. Zheng, *Langmuir*, 23 (2007) 4892.
9. S. H. Li, S. B. Zhang, X. H. Wang, *Langmuir*, 24 (2008) 5585.
10. W. Barthlott and C. Neinhuis, *Planta*, 202 (1997)1
11. X. Gao and L. Jiang, *Nature*, 432 (2004) 36.

12. Y. Zheng, X. Gao, and L. Jiang, *Soft Matter.*, 3 (2007) 178.
13. T. Liu, Y. Yin, S. Chen, X. Chang, and S. Cheng, *Electrochim. Acta*, 52 (2007) 3709.
14. H. Gau, S. Herminghaus, P. Lenz, and R. Lipowsky, *Science*, 283 (1999) 46.
15. D. Quéré, *Rep. Prog. Phys.*, 68 (2005)2495.
16. K. Satoh and H. Nakazumi, *J. Sol-Gel Sci. Technol.*, 27 (2003)327.
17. T. Kako, A. Nakajima, H. Irie, Z. Kato, K. Uematsu, T. Watanabe, and K. Hashimoto, *J. Mater. Sci.*, 39 (2004) 547.
18. L. Feng, S.H. Li, Y.S. Li, H.J. Li, L.J. Zhang, and J. Zhai, *Adv. Mater.*, 14 (2002) 1857.
19. N. Gao, Y.Y. Yan, X.Y. Chen, and D.J. Mee, *Mater. Lett.*, 65 (2011) 2902.
20. Q.P. Ke, W.Q. Fu, H.L. Jin, L. Zhang, T.D. Tang, and J.F. Zhang, *Surf. Coat. Tech.*, 205 (2011) 4910
21. Z.Q. Yuan, J.Y. Xiao, J.C. Zeng, C.Q. Wang, J. Liu, and S.L. Xing, *Surf. Coat. Tech.*, 205 (2010) 1947.
22. V.V. Ganbavle, U.K.H. Bangi, S.S. Latthe, S.A. Mahadik, and A.V. Rao *Surf. Coat. Tech.*, 205 (2011) 5338.
23. H. Yang, X.J. Zhang, Z.Q. Cai, P.H. Pi, D.F. Zheng, X.F. Wen, J. Cheng, and Z.R. Yang, *Surf. Coat. Tech.*, 205 (2011) 5387.
24. Z.Q. Yuan, H. Chen, J.X. Tang, X. Chen, D.J. Zhao, and Z.X. Wang, *Surf. Coat. Tech.*, 201 (2007) 7138.
25. H. Jin, M. Kettunen, A. Laiho, H. Pynnöone, J. Paltakari, A. Marmur, O. Ikkala, and R.H.A. Ras, *Langmuir*, 27 (2011) 1930.
26. N.D. Boscher, P. Choquet, D. Duday, and S. Verdier, *Surf. Coat. Tech.*, 205 (2011) 5350
27. P.R. Roberge, *Handbook of Corrosion Engineering*, McGraw-Hill, New York (1999).