Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Journal of
Materials Chemistry A

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ARTICLE

Creating Superhydrophobic Mild Steel Surfaces for Water Proofing and Oil-Water Separation

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A simple and inexpensive two-step immersion method is reported to make mild steel superhydrophobic. Micro-nano-scale roughness and surface chemistry modifications were created via immersing mild steel into a salt solution followed by treatment with a low surface-energy polymer. The fabricated mild steel has water contact angles greater than 150° and remarkable water bouncing properties. This method was also used to treat a mild steel mesh for oil-water separation. In this paper, a new, facile and reusable gravity-induced separation system is proposed to collect floating oil, the oil collection rate can reach > 96%.

Introduction

Mild steel is the most widely used form of steel because its price is relatively low while it provides material properties that are acceptable for many applications,[1] however, billions of pounds are paid for repair or replacement of rusted mild steel every year. It has been widely accepted that atmospheric corrosion of mild steel is due in part because of contact with air and moisture [2, 3]. Since it is more difficult to protect mild steel from air, research has focused on making mild steel water repellent.

In nature, many objects are water-proof such as Lotus leaves[4], water strider legs[5], and bird's feathers[6]. These surfaces, often demonstrate superhydrophobicity, that is a surface that has a static water contact angle greater than 150°, as well as a dynamic functional property – water bouncing. When a water droplet impacts the superhydrophobic surface from a certain height, it will bounce up without wetting the surface[7]. Inspired by nature, research has focused on preparing artificial superhydrophobic surfaces [8-10] for both fundamental research and industrial applications, such as self-cleaning [11, 12], drag-reduction [13, 14], anti-corrision [15, 16] and anti-oxidation [17, 18]. In this paper, superhydrophobic surfaces were created on mild steel to make it water repellent. It is generally accepted that superhydrophobic surfaces depend on the combination of rough micro-nano-scale structures together with low surface energy modifications. We have fabricated superhydrophobic surfaces on metals via electrochemical methods for surface roughness followed by treatment with a fluorinated polymer [19-21], we found this method has a restricted shape requirement to the electrodes and can only prepare limited shapes and sizes of superhydrophobic surfaces. A chemical immersion method was also developed to fabricate superhydrophobic coatings on steel substrates by a displacement reaction producing a Cu layer with micro-nano-sized structures on the steel substrate [22], this type can fabricate superhydrophobic surfaces on various shapes of substrates such as plates, cylinders and meshes, and however,

the formed Cu layer is not as robust as etched substrates. Qu et al. [23] fabricated superhydrophobic surfaces by immersing steel into a mixed solution of HNO_3 and H_2O_2, followed by immersion in a hydrolyzed silane solution; He et al. [24] used HNO_3 and H_2O_2 as well as stearic acid to make superhydrophobic steel; Hess et al. [25] used a 48–51% hydrofluoric acid solution to etch steel and make superhydrophobic surfaces. Wang et al. [26-28] also designed a series of acidic immersion methods to fabricate superhydrophobic surfaces on metal substrates. All the aforementioned chemical immersion methods used acids to etch rough micro-nano-scale structures on steel substrates; however the acids volatilize in the air and have an impact to the environment and human health, which may hinder large scale industrial productions and applications.

Oil-water separation is another significant application of superhydrophobic surfaces, which are usually made into meshes, gauzes and membranes[29-41] to let oil pass through and stop water.

In this paper, we firstly devised a facile chemical immersion method to etch micro-nano-sized structures on mild steel using a salt solution, followed by low surface energy modifications to fabricate a superhydrophobic surface. This new method can be used for water proofing mild steel to create a surface with a water contact angle larger than 150° as well as remarkable water bouncing properties. Secondly, we used this method to make superhydrophobic mild steel meshes and designed a gravity-induced system to collection oil in oil-water mixtures. This collection system can be reused and the oil collection rate can reach > 96%.

Experimental

Materials: Mild steel (plates and cylinders) was purchased from Goodman. Mild steel woven mesh (0.16 mm diameter) was purchased from Mesh UK. Corn oil was purchased from Waitrose for oil-water separation test. Cupric chloride (98.0%

CuCl$_2$·2H$_2$O) was purchased from BDH Chemicals Ltd. 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (C$_8$F$_{13}$H$_4$Si(OCH$_2$CH$_3$)$_3$) was purchased from Sigma-Aldrich. SYLGARD 184 Silicone Elastomer was purchased from Sigma-Aldrich. Laboratory solvents were purchased from Fisher Scientific and of the highest possible grade. All chemicals were analytical grade reagents and were used as received.

Micro nano sized structure preparation: mild steel plates and meshes were immersed into a CuCl$_2$ (0.2 mol/L) solution for 3 min, followed by being ultrasonically cleaned in distilled water for 30 min, then removed and dried at 90 °C for 1 hour.

Surface energy reduction: The aforementioned sample was immersed in a FAS ethanol solvent (1.0 wt % 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane in absolute ethanol solvent) and SYLGARD 184 Silicone Elastomer (this elastomer consists of two parts, the first is the elastomer and the second a curing agent to encourage cross linking and hardening to generate a heat resistant polymer). Both polymer and cross link agent (10:1 ratio) were dissolved in chloroform (50 mL) by rapid stirring for 5 min[42], respectively, for 2 hours, and then removed, and dried for 2 hours at 90 °C.

Surface characterizations: Scanning Electron Microscopy (SEM) was performed to determine surface morphology using a JEOL JSM-6301F Field Emission SEM. Surface chemical compositions were investigated using an X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-alpha photoelectron spectrometer) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, BRUKER, platinum-ATR, measurements were taken over a range of 1000 to 4000 cm^{-1}). The water contact angles were measured at ambient temperature via the sessile-drop method using an optical contact angle meter (FTA 1000, water droplet is 5 µL). Water bouncing and oil water separation videos were taken by a high speed camera (Casio Ex-fh25).

Water bouncing tests: 1. Water repellent tests were carried on the treated steel cylinder using a 1-mL syringe without a dispensing tip. 2. Water bouncing at different impacting velocities. Water droplets were dropped from heights of 10, 30, 50, 60 and 100 cm using a 1-mL syringe fitted with a 30 gauge dispensing tip to the treated steel plate. The water droplets from this tip were 10 microlitres in size. Methylene blue and orange were added to the water to aid visualisation; this did not change the behaviour of the water droplets on the surface.

Surface robustness test: The treated mild steel plate was longitudinally and transversely abraded by a sand paper (Grade Grit No. 240), then water dropping test was carried out afterwards using a video camera. After the video, two systematic experiments were performed on this sample. 1. Various weight loads on sand paper— various weights (0, 20 g, 50 g, 80 g and 100 g, respectively) were put on the sample, which was moved for 10 cm on the sand paper longitudinally and transversely (20 cm totally travelled per weight load); water contact angles were measured after each weight test. 2. Circles of mechanical abrasion tests were carried out on the same sample after the weight tests, here we defined one cycle for sample weighing 100 g was moved for 10 cm in the longitudinal and transverse paths respectively (20 cm in total); 30 cycles were tested on the sample and water contact angles were measured after each test.

Oil water separation: superhydrophobic mesh was bent as a 'V' shape in cross section in order to hold water. A mixture composited of random masses of oil and water was poured onto the mesh. A beaker under the mesh was used to collect the oil

separated by superhydrophobic mesh. The collection rate equals the mass of collected oil divided by the mass of oil from the oil-water mixture. The first 10 tests of the fabricated mesh were recorded by video. The separation rate was calculated from an average of 15 repeat experiments.

Results and discussion

The fabrication of superhydrophobic mild steel was a two-step process. Mild steel was firstly etched in CuCl$_2$ solution through a facile metathesis reaction for creating micro and nano scaled roughness; the etched samples were then treated with FAS and SYLGARD 184, respectively for low surface energy modifications. It was found that both steps were required to form a superhydophobic surface.

Fig. 1 shows the side view of SEM images, which compared untreated and salt solution etched mild steel surfaces. The etched surface is more textured than untreated mild steel surface.
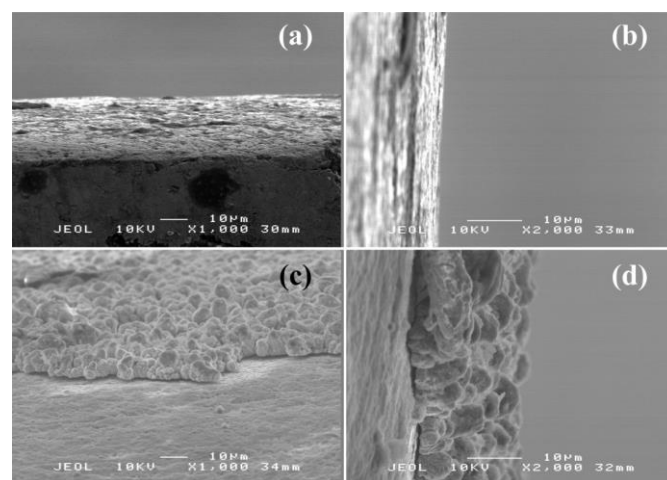
Fig. 1 Side view of SEM images. (a) and (b) show the untreated mild steel surface in 1000 X and 2000 X magnifications, respectively; (c) and (d) show the mild steel surface etched by CuCl$_2$ solution in 1000 X and 2000 X magnifications, respectively.

Fig. 2 (a) and (b) shows the SEM images of surface morphologies of untreated steel at 5000 X and 30000X magnifications respectively. Most areas of the surface were plain and less structured. Fig. 2 (c) and (d) shows the SEM images of mild steel that was etched by CuCl$_2$ solution and then treated with FAS. Micro sized hierarchical structures were present on the surface as shown in Fig. 2(c) while nano sized features were created on the micro sized hierarchical structures as shown in Fig. 2(d). Fig. 2 (e) and (f) shows the SEM images of mild steel which was etched by CuCl$_2$ solution followed by SYLGARD treatment. Micro scaled hierarchical sturctures can also be found in 5000 X magnification, such structures were much more complex than those on untreated mild steel. Bamboo-like nano scaled structures were seen in the 30000 X magnification. Such micro and nano sized hierarchical structures can help support water droplets and are necessary for superhydrophobic surfaces.
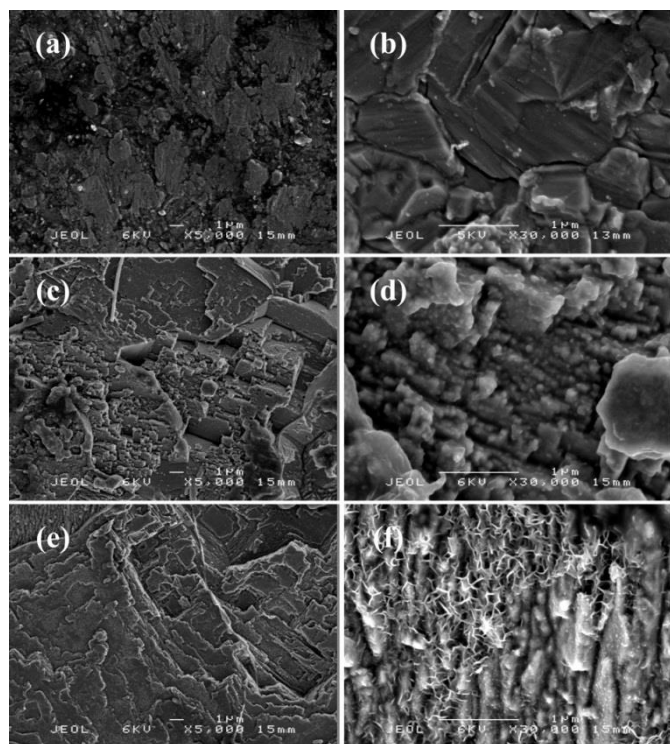
Fig. 2 SEM images of [(a) and (b)] untreated mild steel, [(c) and (d)] mild steel etched by $CuCl_2$ solution followed by FAS modification, [(e) and (f)] mild steel etched by $CuCl_2$ solution followed by SYLGARD treatment. (a), (c) and (e) were in 5000 X magnification while (b), (d) and (f) were in 30000 X magnification.
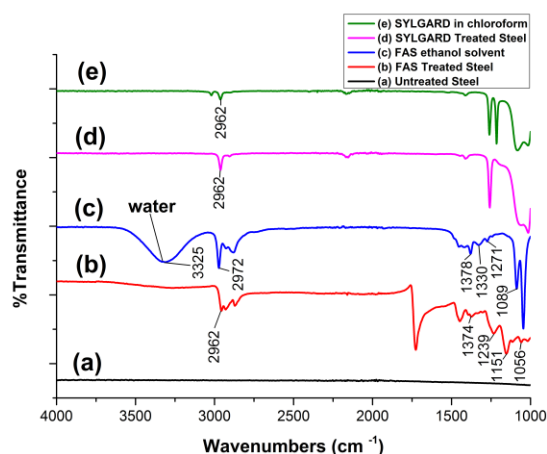
The films were investigated by XPS. Fig. 3 shows the XPS spectra of (a) untreated mild steel, (b) mild steel etched by $CuCl_2$ solution followed by FAS modification and (c) mild steel etched by $CuCl_2$ solution followed by SYLGARD treatment. Elements of Fe (two peaks between 710 and 730 eV), F (between 684 and 692 eV), O (between 528 and 536 eV), C (between 280 and 296 eV), and Si (between 99 and 105 eV) could all be found on both treated and untreated mild steel surfaces. The mild steel intrinsically has elements F, O, C, Si so that the FAS or SYLGARD treatments could not be determined merely by surface element investigation. A further characterization was carried out using ATR-FTIR.
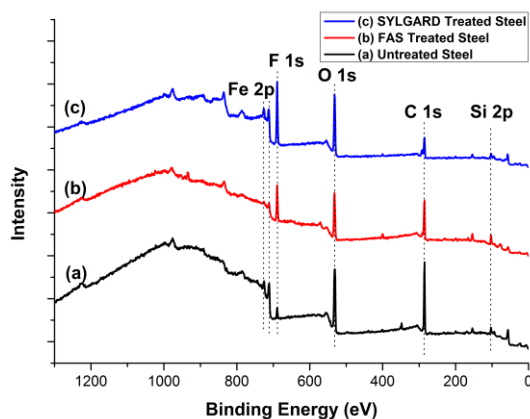
Fig. 3 XPS spectra of (a) untreated mild steel, (b) mild steel etched by $CuCl_2$ solution followed by FAS modification and (c) mild steel etched by $CuCl_2$ solution followed by SYLGARD treatment.

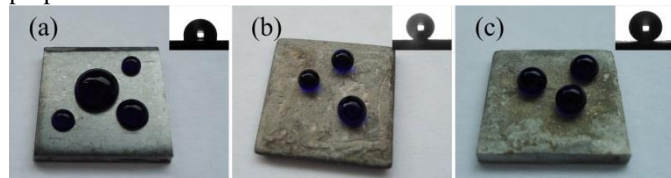Fig. 4 shows ATR-FTIR spectra of (a) untreated mild steel, (b) mild steel etched by $CuCl_2$ solution followed by FAS

modification, (c) FAS ethanol solvent, (d) mild steel etched by $CuCl_2$ solution followed by SYLGARD treatment and (e) SYLGARD in chloroform. No peaks were present on untreated mild steel as shown in Fig. 4 (a), indicating the steel substrate does not contain any detectable organic material. The sample treated with FAS [Fig. 4 (b)] shows absorption bands at 1374, 1239, 1151 cm^{-1} assigned to the C−F stretching vibration of the $-CF_2-$ and $-CF_3$ groups. The peaks at 1056 and 2962 cm^{-1} were assigned to Si−O and C−H chemical bonds, respectively. Fig. 4 (c) shows the ATR-FTIR spectrum of FAS ethanol solvent as comparision, absorption peaks appeared at 1378, 1330, 1271 cm^{-1} corresponding to C−F stretching vibration of the $-CF_2-$ and $-CF_3$ groups, while vibrations were observed at 1089 and 2972 cm^{-1} corresponding to Si−O and C−H chemical bonds, respectively. The peak at 3325 cm^{-1} is due to water. Comparisions among Fig. 4 (a), (b) and (c) illustrate FAS was successfully adhered on $CuCl_2$ solution etched mild steel. Fig. 4 (d) and (e) show the ATR-FTIR spectra of mild steel etched by $CuCl_2$ solution followed by SYLGARD treatment and SYLGARD liquid, respectively, which both have an absorption peak at 2962 cm^{-1} corresponding to C−H vibrations. Comparision of Fig. 4 (d) with Fig. 4 (a/e), it is seen that the SYLGARD has successfully applied to the etched mild steel. Here, only FAS ethanol solvent [Fig. 4 (c)] was detected to contain water among the five graphs, this is due to the ethanol solvent which absorbs moisture from the air. Untreated steel, FAS treated steel and SYLGARD treated steel are shown in Fig. 4 (a) (b) and (d) were dry samples that do not contain water; SYLGARD in chloroform as shown in Fig. 4 (e).

Fig. 4 ATR-FTIR spectra of (a) untreated mild steel, (b) mild steel etched by $CuCl_2$ solution followed by FAS modification, (c) FAS in ethanol solvent, (d) mild steel etched by $CuCl_2$ solution followed by SYLGARD treatment and (e) SYLGARD in chloroform solvent.

A combination of SEM, XPS and ATR-FTIR characterizations show that the micro and nano sized hierarchical structures were created and that low surface energy materials were sucessfully prepared on the surface of mild steel through this new method. The prepared surfaces were superhydrophobic as shown in Fig. 5. Fig. 5 (a) shows water droplets on untreated mild steel that reflects its intrinsical wettability, the water contact angle was 102°. Fig. 5 (b) shows water droplets on the surface of mild steel etched by $CuCl_2$ solution followed by FAS modification, the water contact angle was 156°, indicating this surface is superhydrophobic.[43] Fig. 5 (c) shows water droplets on mild steel etched by $CuCl_2$ solution followed by SYLGARD

treatment, the water contact angle was 157° illustrating the fabricated surface is superhydrophobic. Chemical etching using CuCl$_2$ helps create micro and nano sized hierarchical structures that allow air to be trapped within; FAS or SYLGARD modified film providing a low surface energy on top of the surface roughness. The synthesis effects widen the contact angles on the textured surface and reduce the contact area of the liquid droplets with the surface, resulting in the water repellent properties of the treated mild steel.


Fig. 5 Water droplets on the surface of (a) untreated mild steel, (b) mild steel etched by CuCl$_2$ solution followed by FAS modification and (c) mild steel etched by CuCl$_2$ solution followed by SYLGARD treatment.

The two-step immersion method can be used to treat various shapes of mild steel and make them superhydrophobic. Movie 1 (see supporting information) shows the water droplets dropped on both flat end and curved side of the treated mild steel cylinder. Once a water droplet contacted the surface, it would roll off without sticking. Water bouncing is also an important property of superhydrophobic surfaces. When a liquid drop lands on a solid surface without wetting it, it bounces with remarkable elasticity [7, 44]. Movie 2 (see supporting information) shows the water bouncing test both on the treated and untreated mild steel plate, respectively. Four water bounces happened on the treated mild steel plate from a height of 10 cm, while the water droplet spread out once impacting the surface of the untreated sample. The comparison shows that the treated sample using this method has remarkable water bouncing and water shedding properties - important features for a superhydrophobic surface. Movies 3 to 6 also show that the water droplets impacted the treated surfaces at the impact velocities of 2.4, 3.1, 3.4 and 4.4 m/s, respectively (see supporting information).

The robustness of the treated steel surface was also tested by a sand paper. Movie 7 shows that the surface could stay superhydrophobic after abrasion (see supporting information), indicating this method is effective to create water proofs of mild steel. Fig. S1 (a) shows the water contact angle measurements after the weight load abrasion tests. The surface was still superhydrophobic after weighting 0, 20, 50, 80, 100 g and travelling 10 cm longitudinally and 10 cm transversely. Fig. S1 (b) shows water contact angles after each abrasion cycle. The contact angles decreased gradually and after 30 cycles most of areas of the surface were damaged. The surface robustness is due to the micro structures. Fig. S2 shows SEM images of the surface after 30-cycle mechanical abrasion. There were still some areas showing hydrophobicity as the higher parts of the surface have protected the lower parts, resulting in the lower parts keeping the micro roughness.

Since this chemical immersion method can be used to treat most shapes of mild steel surfaces, we used this method to fabricate a superhydrophobic-superoleophilic mild steel mesh to separate oil in an oil-water mixture. Fig. 6 shows (a) a water droplet and (b) an oil droplet on the fabricated mesh. The water droplet could stay as a marble without wetting the surface, while the oil droplet spread through the mesh resulting in an oil contact angle below 5°. Surfaces like this are usually used for oil-water separations. Fig. 6 (c) and (d) show SEM images of treated and untreated mild steel mesh, respectively. In 50 X and

40000 X magnifications, the treated surface was more structured while the untreated surface was smoother. The differences in surface roughness led to different wettabilities where the treated mild steel mesh showed superhydrophobicity-superoleophilicity, which could be used for oil-water separation.
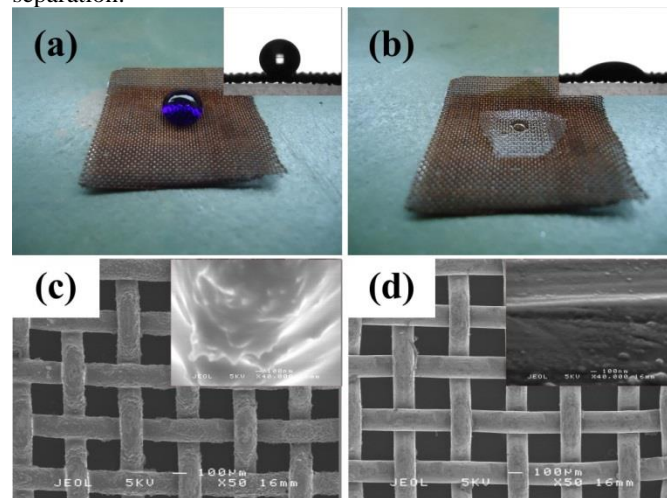
Fig. 6 (a) A water droplet and (b) an oil droplet on superhydrophobic-superoleophilic mild steel mesh. (c) and (d) are SEM images of treated and untreated mild steel mesh in 50 X magnification, respectively. Inserts are in 40000 X magnification.

The oil-water separation systems using superhydrophobic-oleophilic mesh or membrane can be briefly divided into three categories: tube-membrane (or mesh)-container [29-35] [Fig. 7 (a) and (b)], mesh-oil container-water container [36] [Fig. 7 (c) and (d)] and membrane (or mesh) sealed vessel-water container [37-39][Fig. 7 (e) and (f)].
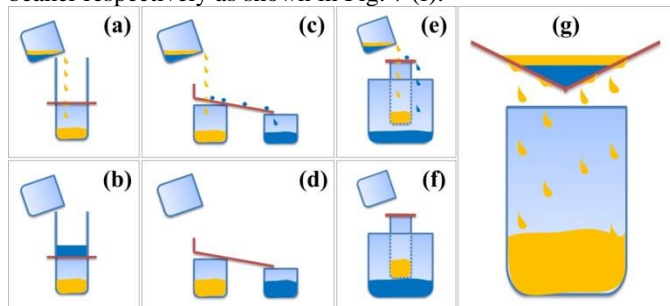
Tube-membrane (or mesh)-container system is a good way to collect heavy oil or heavy organic solvent such as chloroform [30], dichloromethane [31], and heavy crude oil [32]. Heavy oils and organic solvents will stay on the bottom of the tube while water stays on the top to oil-water mixtures above the oils; these conditions enable heavy oils and organic solvents that contact with the separation membranes and pass through. In another case, light oils float on the top-layer of oil-water mixtures must be carefully poured as shown in Fig. 7 (a) so that oils could firstly pass through the mesh and after that water would be stopped and left in the upper tube as shown in Fig. 7 (b). However, for a mixture where oil does not perfectly float on water, or the mixture was poured fast to the tube, there would be some oil left to float on water in the upper tube, resulting in a lower oil-water separation rate or a low oil collection rate. Some researchers have used applied energy to deal with such problems, for example, Tuteja et al. [35] developed a functional membrane whose wettability of oil and water could be controlled by an applied voltage. This design could separate oil-water mixture on demand.

Another example is a mesh-oil container-water container system, which used an inclined superhydrophobic-oleophilic mesh fixed above two beakers as shown in Fig. 7 (c). When the oil-water mixture was poured onto the mesh, oil will pass through the mesh and be collected in the beaker on the left, while water will go along the inclined mesh and roll to the beaker placed at the end of the mesh [36]. After this process, oil and water would be collected in separated beakers as shown in Fig. 7 (d).

The third category [37-39] is to use a superhydrophobic-oleophilic mesh sealed vessel, which is put into a bigger beaker as shown

in Fig. 7 (e). The mixture was poured onto the mesh, oil will go through the mesh and be collected in the vessel while water will be repelled away by the mesh and roll into the bigger beaker, and finally oil and water were contained into the vessel and beaker respectively as shown in Fig. 7 (f).

Fig. 7 Scheme of oil-water separation systems. (a) and (b) refer to tube-membrane (or mesh)-container system; (c) to (f) refer to mesh-oil container-water-container systems. (g) refers to the gravity-induced system developed in this paper. Yellow and blue liquids refer to oil and water, respectively. Here we used the example of light oil floating on water. The meshes or membranes in the middle are superhydrophobic-oleophilic, which can stop water and let oil pass through.

The second and third categories have the similar case as the tube-membrane (or mesh)-container system. Once the mixture was poured quickly, or the oleophilicity of the mesh was not complete, some oil would go with the water droplets and finally get into the water collection container.

Except for systems using superhydrophobic-oleophilic mesh or membrane, there are some other ways using oil absorption materials for oil-water separation. Shen et al.[40] used a superhydrophobic-oleophilic powder to clean up spilt oil in water. They put such powder into an oil-water mixture, then oil was absorbed by the powder and the powder finally sank to the bottom. Pan et al.[41] used superhydrophobic-oleophilic sponges to clean oils from water. These methods could be used for water purity, however, there still requires further steps to separate oil from the powder or sponge.

In this paper, we devised a gravity-induced system for oil-water separation. The fabricated superhydrophobic and superoleophilic mesh was bent into a 'V' shape in cross section (can also be made into baskets, vessels and V-shaped channel etc.), which guaranteed that the floating oils or the oils in the mess and stirred mixtures could always be in contact with the mesh area as shown in Fig. 7 (g). This system could be a supplement of the aforementioned systems and might help a better separation and collection of oil. In addition, no further steps or energy cost were required for oil collection. Movie 8 shows an oil-water separation video with this system.

This system was used for our oil-water separation tests as shown in Table 1. The first ten tests were used for taking pictures and videos. The oil-water separation data was collected from the 11th to 25th separation. The separation rate was the average value of the 15 repeat separation tests, which could reach > 96%. The velocity of oil penetration is 0.3348 g/s in average as shown in Table. S1 (Supporting Information). The system was facile, reusable and had a stable separation rate each time.

Table. 1. Oil water separating tests of the treated mild steel mesh. Here we chose different mass compositions of oil-water mixtures. The separation rate = oil collection (g)/oil (g) x 100%.

Round	Oil (g)	Water (g)	Oil collection (g)	Separation rates
11	20.64	7.95	20.31	98.40%
12	15.99	12.54	15.5	96.94%
13	13.27	11.6	12.69	95.63%
14	13.6	15.35	13.37	98.31%
15	8.94	7.39	8.53	95.41%
16	8.46	6.42	7.97	94.21%
17	7.76	9.18	7.53	97.04%
18	8.42	11.62	8.11	96.32%
19	10.34	7.32	9.86	95.36%
20	9.14	12.06	8.74	95.62%
21	7.27	11.59	6.86	94.36%
22	8.2	10.48	7.72	94.15%
23	9.42	14.5	9.06	96.18%
24	15.05	11.24	14.63	97.21%
25	10.83	12.78	10.71	98.89%

Conclusions

In conclusion, we have fabricated superhydrophobic surfaces on mild steel using a simple and inexpensive two-step chemical immersion method. Immersing mild steel into $CuCl_2$ solution was used to create surface micro and nano sized hierarchical roughness, the salt solution was more environmental friendly than the use of strong acids and was readily removed by washing; FAS or SYLGARD was coated onto the surface by immersion to reduce the surface energy of the textured mild steel. The method can be used to treat mild steel with different shapes (plates, cylinders and meshes). The fabricated mild steel has a water contact angle greater than 150° as well as significant water bouncing properties. This method is readily scalable and could be used on large industrial productions and applications for making mild steel water repellent. We used this method to prepare superhydrophobic-superoleophilic mild steel mesh and built a gravity-induced system to collect oil in oil-water mixtures, the mesh could be reused and the separation rate could reach > 96%.

Acknowledgements

Notes and references

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1   http://en.wikipedia.org/wiki/Carbon_steel.

2   M. Yamashitaa, H. Miyukia, Y. Matsudaa, H. Naganoa, T. Misawa, *Corros. Sci.*, 1994, **36**, 283.

3   T. Misawa, *Corros. Sci.*, 1974, **14**, 279.

4   W. Barthlott and C. Neinhuis, *Planta*, 1997, **202**, 1.

5   X. Gao and L. Jiang, *Nature*, 2004, **432**, 36.

6   C. R. Crick, J. C. Bear , A. Kafizas and I. P. Parkin, *Adv. Mater.* 2012, **24**, 3505.

7   D. Richard, C. Clanet and D. Quéré, *Nature*, 2002, **417**, 811.

8   J. Song, S. Huang, K. Hu, Y. Lu, X. Liu and W. Xu, *J. Mater. Chem. A*, 2013, **1**, 14783.

9   J. Song, H. Liu, M. Wan, Y. Zhu and L. Jiang, *J. Mater. Chem. A*, 2013, **1**, 1740.

10   Q. Zhang, M. He, J. Chen, J. Wang, Y. Song and L. Jiang, *Chem. Commun.*, 2013, **49**, 4516.

11   I. P. Parkin and R. G. Palgrave, *J. Mater. Chem.*, 2005, **15**, 1689.

12   R. Blossey, *Nature Mater.*, 2003, **2**, 301.

13   G. McHale, M. I. Newton and N. J. Shirtcliffe, *Soft Matter*, 2010, **6**, 714.

14   R. Truesdell, A. Mammoli, P. Vorobieff, F. van Swol1 and C. J. Brinker, *Phys. Rev. Lett.*, 2006, **97**, 044504.

15   Q. Xu and J. Wang, *New J. Chem.*, 2009, **33**, 734.

16   W. Xu, J. Song, J. Sun, Y. Lu and Z. Yu, *ACS Appl. Mater. Interfaces*, 2011, **3**, 4404.

17   W. Wu, X. Wang, D. Wang, M. Chen, F. Zhou, W. Liu and Q. Xue, *Chem. Commun.*, **2009**, 1043.

18   J. Yang, Y. Zhou, O. Takeshi, I. Ryoichi and O. Masazumi, *J. Mater. Sci.*, 2007, **42**, 7638.

19   Y. Lu, J. Song, X. Liu, W. Xu, Y. Xing and Z. Wei, *ACS Sustainable Chem. Eng.* 2013, **1**, 102.

20   Y. Lu, J. Song, X. Liu, W. Xu, J. Sun and Y. Xing, *Micro Nano Lett.* 2012, **7**, 786.

21   Y. Lu, W. Xu, J. Song, X. Liu, Y. Xing and J. Sun, *Appl. Surf. Sci.*, 2012, **263**, 297.

22   X. Liu, J. Song, L. Wu, W. Xu, Y. Lu and J. Sun, *Micro Nano Lett.* 2012, **7**, 456.

23   M. Qu, B. Zhang, S. Song, L. Chen, J. Zhang and X. Cao, *Adv. Funct. Mater.* 2007, **17**, 593.

24   Q. Wang, B. Zhang, M. Qu, J. Zhang and D. He, *Appl. Surf. Sci.*, 2008, **254**, 2009.

25   L. Li, V. Breedveld and D. W. Hess, *ACS Appl. Mater. Interfaces*, 2012, **4**, 4549.

26   S. Wang, L. Feng, and L. Jiang, *Adv. Mater.* 2006, **18**, 767.

27   S. Wang, Y. Song and L. Jiang, *Nanotechnology* 2007, **18**, 015103.

28   S. Wang, L. Feng, H. Liu, T. Sun, X. Zhang, L. Jiang and D. Zhu, *ChemPhysChem* 2005, **6**, 1475.

29   J. Li, L. Shi, Y. Chen, Y. Zhang, Z. Guo, B. Su and W. Liu, *J. Mater. Chem.*, 2012, **22**, 9774.

30   B. Wang, J. Li, G. Wang, W. Liang, Y. Zhang, L. Shi, Z. Guo, and W. Liu, *ACS Appl. Mater. Interfaces* 2013, **5**, 1827.

31   Y. Shang, Y. Si, A. Raza, L. Yang, X. Mao, B. Ding and J. Yu, *Nanoscale*, 2012, **4**, 7847.

32   X. Zhang, Z. Li, K. Liu, and L. Jiang, *Adv. Funct. Mater.* 2013, **23**, 2881.

33   Q. Wen, J. Di, L. Jiang, J. Yu and R. Xu, *Chem. Sci.*, 2013, **4**, 591.

34   Y. Cao, X. Zhang, L. Tao, K. Li, Z. Xue, L. Feng, and Y. Wei, *ACS Appl. Mater. Interfaces*, 2013, **5**, 4438.

35   G. Kwon, A. K. Kota , Y. Li , A. Sohani , J. M. Mabry, and A. Tuteja, *Adv. Mater.* 2012, **24**, 3666.

36   Q. Pan, M. Wang, and H. Wang, *Appl. Surf. Sci.*, 2008, **254**, 6002.

37   C. Wang, T. Yao, J. Wu, C. Ma, Z. Fan, Z. Wang, Y. Cheng, Q. Lin, and B. Yang, *ACS Appl. Mater. Interfaces*, 2009, **1**, 2613.

38   C. R. Crick, J. A. Gibbins and I. P. Parkin, *J. Mater. Chem. A*, 2013, **1**, 5943.

39   D. Tian, X. Zhang, X. Wang, J. Zhai and L. Jiang, *Phys. Chem. Chem. Phys.*, 2011, **13**, 14606.

40   T. Arbatan, X. Fang, W. Shen, *Chem. Eng. J.*, 2011, **166**, 787.

41   Q. Zhu, Q. Pan, and F. Liu, *J. Phys. Chem. C*, 2011, **115**, 17464.

42   C. R. Crick and I. P. Parkin, *J. Mater. Chem.*, 2009, **19**, 1074.

43   C. R. Crick and I. P. Parkin, *Chem. Eur. J.*, 2010, **16**, 3568.

44   P. Aussillous and D. Quéré, *Nature*, 2001, **411**, 924.
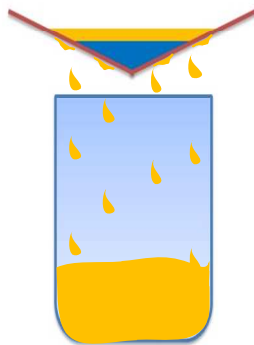
The fabricated superhydrophobic-superoleophilic mesh is bent into a V-shape-channel to guarantee floating oils are always in contact with the mesh.