Facile fabrication of superhydrophobic sand: potential advantages for practical application in oil-water separation

Abstract

Development of cost-effective and **handy** functional materials that can separate oil from water readily **by a convenient method** is highly desirable and still challenge. Herein, sand-based superhydrophobic surfaces were easily achieved by coating sand particles with silane, and the whole fabrication process was time-saving and facile to carry out. The superhydrophobic surfaces can be applied as an oil sorbent scaffold to absorb oil from water selectively because of their water-repelling and oil-attracting properties. Additionally, the time required for oil-water separation was shortened significantly by combining the separation process with a vacuum system. Importantly, the superhydrophobic surfaces can maintain their high selectivity and separation efficiency even after several cycles of oil-water separation, thus providing great potential and advantage for practical application in oil-water separation.

Keywords: superhydrophobic; sand; oil-water separation; recyclability;

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1. Introduction

With increasing occurrence of industrial oily wastewater and oil spill accidents [1-4], developing novel materials that can effectively separate oils from industrial wastewaters, polluted oceanic waters, and oil-spill mixtures is highly desired. Current methods to address this challenge mainly include collection of oil from water surface, mixing of oil with water using dispersing agents to facilitate natural degradation, and in situ burning of oil spills [5]. The collection of oil is often preferred because it allows proper disposal of oil. To enhance recovery of the oil, researchers have mostly commonly developed oil-water separation materials through conferring opposite wetting behavior to water and oil on material substrates [6]; and approaches adopted to realize this goal include mold pressing [7, 8], phase separation [9], dip coating [10-13], chemical vapor deposition [14], wet-chemical method [15] and others [16-26]. However, some of the materials usually required complicated and expensive fabrication procedures, while others displayed limited reusability. These limitations severely hindered their use in practical applications. Generally, an ideal oil-water separation material should have the properties such as facile fabrication process, low cost, high selectivity, excellent recyclability, environmentally benign, and so on. Moreover, speed and efficiency for oil-water separation are also key factors for practical applications and should be considered into fabrication of the materials.

Sand, one of the raw materials in nature, offers benefits of rich source, low cost, and nontoxicity to environment, and thus is a good candidate to construct oil-water separation materials. In this study, we developed a facile approach to fabricate a

sand-based superhydrophobic surface applied for oil-water separation by coating sand particle surfaces with silane. Our strategy to design the superhydrophobic surface with performance of oil-water separation is shown in Fig. 1. The whole procedure was conducted under a mild environment, and no intricate instruments and expensive chemicals were needed. It is noteworthy that nonfluorinated dispersion for the formation of functional sand was used during the procedure, which has low environmental impact and shows definitely environmentally benign. Water droplets could roll off the obtained surface easily, while organic liquids such as hexadecane wet it completely. The application of the functional sands was demonstrated by separating oils from water surface efficiently. In addition, the speed for oil-water separation can be improved significantly, when applied in conjunction with a vacuum system. Moreover, the applied scale for oil-water separation can be controlled easily via adjustable usage amount of the functional sands. In general, micro/nanostructures of many superhydrophobic surfaces are easily destroyed under atrocious weather or other conditions, therefore leading to permanent destruction of the surface superhydrophobicity. However, unlike the conventional materials, the surface wettability of our functional sands was retained after molding sand into any shape due to random accumulation of the sand particles. More importantly, no complicated apparatus or expensive materials are required, which can significantly decrease material and operating cost of the oil-water separation. Therefore, we hope this study could contribute to the development of advanced oil-water separation materials for practical applications.

Fig. 1. Schematic illustration of fabrication process and oil-water separation of the superhydrophobic sand.

2. Experimental

2.1 Materials

Octadecyltrichlorosilane was provided by Shanghai Boer Chemical Reagent Co., Ltd., China. Hexadecane and chloroform were provided by Tianjin Kermel Chemical Reagent Co., Ltd., China. Commercially available sand (diameter: 100 ~ 500 μm) was purchased from a local store and was cleaned with ethanol and deionized water sequentially in an ultrasonic cleaner before use. The other chemicals are of analytical grade and used as received.

2.2 Surface functionalization of sand particles

10 g sand was ultrasonically dispersed in 200 ml toluene, and 10 ml of octadecyltrichlorosilane was added dropwise under stirring at ambient temperature. The reaction mixture was stirred at ambient temperature for 2 h. Finally, the resultant suspension was centrifuged and placed to dry in an oven for 30 min at 80 $^{\circ}\text{C}$ to obtain

the functional sand particles (hydrophobic).

2.3 oil-water separation test

For oil-water separation, a filter module composed of the functional sand and cotton is fixed into a cone-shaped funnel; and a mixture of distilled water (dyed with methylene blue) and chloroform (colored with oil red O) was poured into the filter module, and spontaneously separated. In addition, in order to shorten the time requiring for oil-water separation, the filter flask is connected with vacuum pump (SHZ-D (III), China) by rubber pipe.

2.4 Characterization

Contact angle (CA) and sliding angle (SA) measurements were performed using a KRÜSS DSA 100 (KRÜSS Company, Ltd., Germany) apparatus at ambient temperature. The volume of water and oil droplet in each measurement was 5 μL . Scanning electron microscopy measurements were carried out using a JSM-6701F field-emission scanning electron microscopy (FESEM, JEOL, Japan). Fourier transform infrared (FTIR) spectra were collected on a Bruker IFS66 V/S spectrometer. Thermal measurement was carried out using a thermogravimetric analysis instrument (TGA, PerkinElmer PE7) under air atmosphere at a rate of 10 $^{\circ}\text{C}/\text{min}$. The optical images were captured by a digital camera (Canon).

3. Results and discussion

Fig. 2 shows surface morphology of the sands before and after coating with silane.

Sand particles collision with each other under vigorous stirring leading to the average diameter of modified sands became smaller compared with original sand (Fig 2A and

B). EDS spectra (Fig. 2C and D) were employed to investigate the composition difference of the sand before and after functionalization. Compared with the pristine sand, the content of carbon in EDS spectra of the functional sand increases greatly, indicating that the silane was successfully coated on surfaces of the sand particles.

Fig. 2. SEM images of the sand before (A) and after (B) coating with silane; EDS spectra of the sand before (C) and after (D) coating with silane.

FTIR analysis shows that two absorption peaks positioned at 2922 cm^{-1} and 2850 cm^{-1} appeared which was corresponding to stretching vibration of $-\text{CH}_3$ group (see Fig. 3A). This result indicates that alkyl group has been successfully attached on the sand surface. Moreover, we also investigated the content of silane modified on the surface. TGA analysis indicates that the content of it on the sand surface is about 3.84 wt%, as shown in Fig. 3B. The coated silane significantly lowers the surface energy of the sand surface. This low surface energy, combined with the rough surface texture, led to the silane coated surface exhibit superhydrophobic property. For further understanding of thermal stability of the superhydrophobic surface, related measurements were investigated (Fig. S1), and results showed that the surface wettability was changed gradually from superhydrophobicity to hydrophobicity when the temperature is above

200 °C.

Fig. 3. A. FTIR analysis of the sand before (line 1) and after (line 2) coating with silane; B. TGA thermograms of the pristine sand (line 1) and the silane coated sand (line 2).

The pristine sand sank underwater, while the functional sand floated on the water surface without sinking, owing to its water-repelling property (see Fig. S2). **Small droplet of water with a volume of 5 μ L almost appeared to a sphere on the superhydrophobic surface.** The bright, reflectively visible surface underneath the water droplet in Fig. 4A was a signature of trapped air and the establishment of a composite solid-liquid-air interface [27]. Formation of this composite interface enhanced the surface super-repellence by promoting the high CA (advancing contact angle $\theta_a = 154.8 \pm 1.0^\circ$, receding contact angle $\theta_r = 153.2 \pm 1.1^\circ$) and a low SA of $4.5 \pm 0.9^\circ$ (see Fig. 4B and C, Table S1). On the contrary, the hexadecane droplet can wet the superhydrophobic surface completely and spread out the surface immediately, within the time of 0.7s, as shown in Fig. 4D-E. Interestingly, it can be seen that the superhydrophobicity of our functional sands was retained after molding sand into any shape due to random accumulation of the sand particles (Fig. 4F), and the advantage is distinct from many other materials for oil-water separation, which can be

anticipated to decrease material and operating costs.

Fig. 4. A. Optical image of water (dyed with methylene blue) and hexadecane (dyed with oil red O) placed on the sand surface; B and C is the contact angle and sliding angle profile of water droplet, respectively; D-E. Spreading and permeating behavior of hexadecane droplet. A hexadecane droplet spreads immediately on the superhydrophobic sand surface within 0.7 s. F. Water droplets on superhydrophobic sands with random surfaces.

The surface of the functional sand possessed superhydrophobic and superoleophilic properties simultaneously, allowing it to be an ideal candidate for removing oil from water. When brought into contact with an oil film spreading on a water surface, the sand particles instantaneously absorbed the oil contacting with them, **resulting in a cleaned water surface** (Fig. 5A-C). More importantly, all the oil absorbed in the sand could be extracted by immersing the oil-soaked sand into acetone. In this way, the superhydrophobic surfaces can be reused for oil-water separation time and time again.

1 Interestingly, the sands encapsulated by the oil bead up on the bottle bottom (see
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3 Fig. 5D), which was referred as an oil marble, corresponding to the liquid marble of a
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5 liquid encapsulated by hydrophobic particles in air [28]. Reported liquid marbles
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7 mainly focused on fabricating water marbles, which can float on or be immersed in
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9 other liquids [29]. Oil marbles in air have been demonstrated using Janus particles
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11 [30], however, such effect of oil spheres forming under water encapsulated by
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13 superhydrophobic particles is not as well documented [31]. It was assumed that this
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15 liquid-liquid separation took place under the consideration of minimizing the surface
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38 **Fig. 5.** Optical images for removal of the hexadecane film (dyed with oil red O)
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40 spreading on the water surface using the as-prepared hydrophobic sand.
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43 Separation of oil pollutants from water via a fast way became an urgent demand
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45 in practical application. Herein, a filter module (Fig.S3) composed of the functional
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47 sands and the cotton is fixed into a cone-shaped funnel and is used to separate the
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49 oil-water mixture. A faster oil-water separation occurred when the vacuum system
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51 was introduced. As shown in Fig. 6, when the mixture of 0.05 M AgNO_3 aqueous
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53 solution (15 ml, dyed with methylene blue) and chloroform (25 ml, dyed with oil red
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55 O) was poured onto the filter, the chloroform penetrated the filter and flowed down
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the bottle underneath whereas the water retained on the surface of the filter. Afterwards, the oil was continuously pumped into the bottle under the vacuum of 0.05 MPa, and finally no water exists in the collected oil. The total time for separation of the oil-water mixture was merely about 20 s, in contrast, the time needed for the filtration of the same volume without vacuum system is 7 minutes 23 seconds, so this improved separation speed may potentially expand the application of the functional sand in the field of oil-water separation.

Fig. 6. A The separation apparatus equipped with a vacuum system was used to oil-water separation. The inset shows the magnified image of the separation module, (a and b stands for the superhydrophobic sand and cotton, respectively); B-D Chloroform permeates through while water retains above the separation apparatus after 20s. For easy observation, the water (AgNO_3 aqueous solution) and oil (chloroform) was dyed with methylene blue and oil red O, respectively.

We next investigated the separation efficiency of the filter. It is well known that Ag^+ is very sensitive to Cl^- . Even if a tiny amount of Ag^+ was contact with the Cl^- , a

white precipitate would generate. It was found that no white precipitate was observed, when NaCl aqueous solution (0.1 M) was poured into the beaker containing chloroform separated by the filter, indicating the high oil-water separation efficiency of the filter (see Fig. 7A). Importantly, the filter can retain its high separation efficiency even after five cycles of oil-water separation, as shown in Fig. 7B. Thus, the as-prepared superhydrophobic surface is a good candidate in industrial oil-polluted water treatment and oil spill cleanup.

Fig. 7. Collected oil (chloroform, colored with oil red O) in a beaker containing 0.1 M NaCl aqueous solution. The oil shown in image A and B was separated from oil-0.05 M AgNO₃ aqueous solution using superhydrophobic sand after one and five separation cycles, respectively.

4. Conclusion

Sand-based superhydrophobic surfaces used for oil-water separation were fabricated by modifying the sand surfaces with silane. Water droplets exhibit spherical shape on the superhydrophobic surface, while organic liquids such as hexadecane can wet it completely. Exploiting its oil attracting and water repellency properties, the obtained functional sand is demonstrated as an oil sorbent scaffold in water. When combined with a vacuum system, the time required for oil collection was significantly

1 shortened. The superhydrophobic surfaces can keep its high separation efficiency after
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3 five cycles of oil-water separation, demonstrating its good reusability. Our approach
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5 to develop the sand-based superhydrophobic surfaces applied to oil-water separation
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8 offers benefits of simplicity, cost efficiency, improved separation speed, and good
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10 reusability and is hoped to provide a promising candidate for separation large-scale
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13 oils from water.
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17 **Supporting Information**

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20 Experimental details and further information of characterization are available on the
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22 supporting information section.
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References

- [1] Shannon MA, Bohn PW, Elimelech M, Georgiadis BJ, Marinas AM. Science and technology for water purification in the coming decades. *Nature* 2008;452:301-10.
- [2] Choi HM, Cloud RM. Natural sorbents in oil spill cleanup. *Environ Sci Technol* 1992;26:772-76.
- [3] Chang YC, Wang N, Durak OS. Ship recycling and marine pollution. *Mar Pollut Bull* 2010;60:1390-95.
- [4] Feng L, Zhang ZY, Mai ZH, Ma YM, Liu BQ, Jiang L, Zhu DB. A Super-hydrophobic and super-oleophilic coating mesh film for the separation of oil and water. *Angew Chem Int Ed* 2004;43:2012-14.
- [5] Korhonen JT, Kettunen M, Ras RHA, Ikkala O. Hydrophobic nanocellulose aerogels as floating, sustainable, reusable, and recyclable oil absorbents. *ACS Appl Mater Interfaces* 2011;3:1813-16.
- [6] Kota AK, Kwon G, Choi W, Mabry JM, Tuteja A. Hygro-responsive membranes for effective oil–water separation. *Nat. Commun.* 2012;3:1025-12.
- [7] Zhang X, Guo YG, Chen HZ, WZ Zhu, Zhang PY. A novel damage-tolerant superhydrophobic and superoleophilic material. *J. Mater. Chem. A* 2014;2:9002-06.
- [8] Ge B, Zhang ZZ, Zhu XT, Ren GN, Men XH, and Zhou XY. A magnetically superhydrophobic bulk material for oil removal. *Colloids Sur A* 2013;429:129-33.
- [9] Xue ZX, Sun ZX, Gao YZ, Chen YN, Tao L, Li K, Feng L, Fu Q, Wei Y. Superoleophilic and superhydrophobic biodegradable material with porous structures for oil absorption and oil-water separation. *RSC Adv* 2013;3:23432-37.

- [10] Wu L, Li LX, Li BC, Zhang JP, Wang AQ. Magnetic, durable, and superhydrophobic polyurethane@Fe₃O₄@SiO₂@fluoropolymer sponges for selective oil absorption and oil/water separation. *ACS Appl. Mater. Interfaces* 2015;7:4936-46.
- [11] Zhu XT, Zhang ZZ, Ge B, Men XH, Zhou XY, Xue QJ. A versatile approach to produce superhydrophobic materials used for oil-water separation. *J Colloid Interface Sci* 2014;432:105-8.
- [12] Liu SH, Xu QF, Latthe SS, Gurav AB, Xing RM. Superhydrophobic/superoleophilic magnetic polyurethane sponge for oil/water separation. *RSC Adv.* 2015;5:68293-98.
- [13] Patowary M, Ananthakrishnan R, Pathak K. Chemical modification of hygroscopic magnesium carbonate into superhydrophobic and oleophilic sorbent suitable for removal of oil spill in water. *Appl Surf Sci* 2014;320:294-300.
- [14] Cui XC, Wei JQ, Wang KL, Cao AY, Zhu HW, Jia Y, Shu QK, Wu D.H. Carbon nanotube sponges. *Adv Mater* 2010;22:617-21.
- [15] Basu M, Sinha A K, Pradhan M, Sarkar S, Negishi Y, Pal T. Fabrication and functionalization of CuO for tuning superhydrophobic thin film and cotton wool. *J. Phys. Chem. C.* 2011;115:20953-63.
- [16] Gao SJ, Shi Z, Zhang WB, Zhang F, Jin J. Photoinduced superwetting single-walled carbon nanotube/TiO₂ ultrathin network films for ultrafast separation of oil-in-water emulsions. *ACS Nano* 2014;8:6344-52.
- [17] Wang FJ, Lei S, Xue MS, Ou JF, Li CQ, Li W. Superhydrophobic and superoleophilic miniature device for the collection of oils from water surfaces. *J Phys*

Chem C 2014;118:6344-51.

[18] Wang G, Zeng ZX, Wu XD, Ren TH, Han J, Xue QJ. Three-dimensional structured sponge with high oil wettability for the clean-up of oil contaminations and separation of oil-water mixtures. Polym Chem 2014;5:5942-48.

[19] Zhang Z, Sèbe G, Rentsch D, Zimmermann T, Tingaut P. Ultralightweight and flexible silylated nanocellulose sponges for the selective removal of oil from water. Chem. Mater. 2014; 26, 2659-68.

[20] Dai C N, Liu N, Cao Y Z, Chen Y N, Lu F, Feng L. Fast formation of superhydrophobic octadecylphosphonic acid (ODPA) coating for self-cleaning and oil/water separation. Soft Matter, 2014;10:8116-21

[21] Guo W, Zhang Q, Xiao HB, Li QT, Pan XH, Huang ZY. Cu mesh's super-hydrophobic and oleophobic properties with variations in gravitational pressure and surface components for oil/water separation applications. Appl Surf Sci 2014;314:408-14.

[22] Zhu Q, Pan QM. Mussel-inspired direct immobilization of nanoparticles and application for oil-water separation. ACS Nano 2014;8:1402-09.

[23] Gu JJ, Jiang W, Wang FH, Chen MD, Mao JY, Xie T. Facile removal of oils from water surfaces through highly hydrophobic and magnetic polymer nanocomposites. Appl Surf Sci 2014;301:492-9.

[24] Nadargi D, Gurav J, Marioni MA, Romer S, Matam S, Koebel MM. Methyltrimethoxysilane (MTMS)-based silica-iron oxide superhydrophobic nanocomposites. J Colloid Interface Sci 2015;459:123-6.

- [25] Zang DL, Liu F, Zhang M, Gao ZX, Wang CY. Novel superhydrophobic and superoleophilic sawdust as a selective oil sorbent for oil spill cleanup. *Chem Eng Res Des* 2015;102:34-41.
- [26] Sun XC, Liu YX, Mopidevi S, Meng YT, Huang F, Parisi J, Nieh MP, Cornelius C, Suib SL, Lei Y. Super-hydrophobic “smart” sand for buried explosive detection. *Sens Actuators B* 2014;195:52-7.
- [27] Cassie ABD, Baxter S. Wettability of porous surfaces. *Trans Faraday Soc* 1944;40:546-51.
- [28] Aussillous P, Quere D. Liquid marbles. *Nature* 2001;411:924-27.
- [29] Xue YH, Wang HX, Zhao Y, Dai LM, Feng LF, Wang XG, Lin T. Magnetic liquid marbles: a “precise” miniature reactor. *Adv Mater* 2010;22:4814-18.
- [30] Kim SH, Lee SY, Yang SM. Janus microspheres for a highly flexible and impregnable water-repelling interface. *Angew Chem Int Ed* 2010;49:2535-58.
- [31] Zhang L, Wu JJ, Wang YX, Long YH, Zhao N, Xu J. Combination of bioinspiration: a general route to superhydrophobic particles. *J Am Chem Soc* 2012;134:9879-81.

Graphical Abstract

Superhydrophobic sand surface that can separate oil from water efficiently was
fabricated by a facile approach.