Chemical Engineering Journal 166 (2011) 787–791

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Short communication

Superhydrophobic and oleophilic calcium carbonate powder as a selective oil sorbent with potential use in oil spill clean-ups

Tina Arbatan[a], Xiya Fang[b], Wei Shen[a,*]

[a] Australian Pulp and Paper Institute, Department of Chemical Engineering, Monash University, Wellington Road, Clayton, Victoria 3800, Australia
[b] Monash Center for Electron Microscopy, Monash University. Wellington Road, Clayton, Victoria 3800, Australia

ARTICLE INFO

Article history:
Received 1 September 2010
Received in revised form 3 November 2010
Accepted 3 November 2010

Keywords:
Superhydrophobic
Oleophilic
Calcium carbonate
Powder
Oil sorbent
Oil spill control

ABSTRACT

Catastrophic oil spills such as that in Gulf of Mexico remind us of the necessity of prompt action to develop an environmentally friendly, cost-effective, and large-scale technology to minimize environmental consequences caused by such disasters. The feasibility of using superhydrophobic and oleophilic mineral powders to selectively absorb oil from water is thus of great interest. In this communication we report the preparation, characterization and laboratory testing of superhydrophobic calcium carbonate powder treated with fatty acid as selective oil sorbent to separate oil from an oil–water mixture.

1. Introduction

Changing the wetting behaviour of a surface may potentially result in novel materials possessing extraordinary characteristics. For instance, a superhydrophobic surface which is generally considered as a surface demonstrating a high level of water repellency, can be obtained if certain hierarchical roughness of micron and sub-micron size can be created on a low surface energy substrate [1,2]. According to the Cassie–Baxter model (Eq. (1)) [3], introducing a dual-scale roughness to a solid surface can significantly reduce the fraction of the contact area between the solid surface and a contacting liquid drop (ϕ) while increasing the fraction of air–liquid interface due to the air entrapment in the surface structure. In this model, $\theta_{\text{Cassie–Baxter}}$ is the apparent contact angle on the rough surface while $\theta_{\text{Intrinsic}}$ is the intrinsic contact angle on a smooth surface of identical chemical composition. It has been shown that an omniphobic surface, i.e. a surface that repels both water and low surface tension organic liquid, can be created by considering a third factor – the liquid re-entrant surface curvature [4]. As a facile method of investigation of wetting behaviour, water contact angle and the contact angle hysteresis are measured. For superhydrophobic surfaces, a water contact angle higher than 150° and a contact angle hysteresis of below 5° are expected [5,6].

$$\cos\theta_{\text{Cassie–Baxter}} = \phi(\cos\theta_{\text{Intrinsic}} + 1) - 1 \qquad (1)$$

Several distinctive characteristics have been investigated so far for superhydrophobic surfaces; these include self-cleaning properties, fluidic drag reduction, and anti-fouling properties, just to name a few [7–9]. Amongst all of the potential applications, oil and water separation is definitely one of the most interesting.

Most superhydrophobic surfaces that are fabricated without considering the liquid re-entrant surface curvature are not resistant to liquids of low surface tension [4], and are therefore oleophilic. This property of superhydrophobic surfaces has been reportedly highly useful in oil and water separation using superhydrophobic meshes [10–20]. It is thus feasible to use a superhydrophobic powder as an oil-sorbent to selectively absorb oil out of a water–oil mixture.

A superhydrophobic and oleophilic powder mass may be seen as a capillary matrix; the Washburn equation [21] (Eq. (2)), which was initially proposed to model liquid penetration in a single cylindrical capillary tube, can be used to provide the first order description of the absorption behaviour of oil and water into the capillary matrix of a porous material.

$$L^2 = \frac{\gamma D \cos\theta t}{4\eta} \qquad (2)$$

In Eq. (2), D is the representative diameter of the capillary, L is the liquid penetration distance along a capillary in time t, γ and η are the liquid surface tension and viscosity, θ is the contact angle for

---

* Corresponding author. Tel.: +61 3 99053447.
E-mail address: Wei.shen@eng.monash.edu.au (W. Shen).

1385-8947/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.11.015

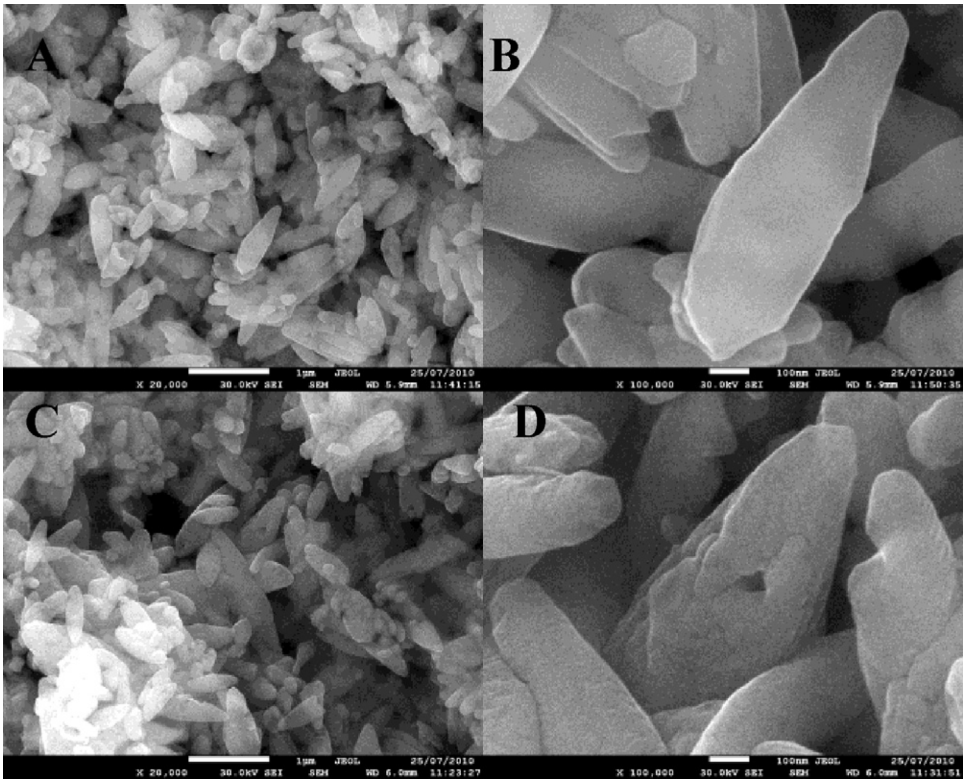

Fig. 1. SEM images of the porous structure of Precarb 100. (A) and (B) before the treatment with fatty acid; (C) and (D) after treatment with fatty acid.

the liquid on the solid surface. According to the Washburn equation, the liquid contact angle is the critical parameter, which controls oil and water separation, since $\theta = 90^\circ$ is the dividing point of liquid penetration into or rejection by the capillary matrix.

In this report we have prepared and characterized superhydrophobic precipitated calcium carbonate powder (PCC) via treatment with stearic acid and used the prepared powder to selectively absorb diesel and crude petroleum oil out of water–oil mixture. Such a simple powder system has provided encouraging results in our preliminary investigation.

2. Experimental

2.1. Chemicals and materials

A precipitated calcium carbonate powder, Precarb 100, was purchased from BASF. It is inherently hydrophilic and porous and has a bulk density of 0.5 g/ml according to the manufacturer's specifications. Stearic acid, sodium hydroxide and the Sudan (IV) dye were acquired from Aldrich. Diesel oil was purchased from a local Shell gas station and crude oil was kindly provided by Shell Refining (Australia) Pty Ltd. Its detailed composition was kindly supplied by the Shell Refining as follows: 50% Mudi Indonesia; 42% Cendor Malaysia; 4% SLEB Brunei; 2.7% Jabiru Australia; 1.3% Challis Australia. MilliQ water was used in all the qualitative and quantitative experiments.

2.2. Fatty acid treatment of PCC

In a typical reaction [20], 20 g of Precarb 100 was dispersed in 50 g of water in a beaker; the beaker was kept at 100 °C and constantly stirred. In a second beaker, 1 g stearic acid was added to 20 g of water plus 2 droplets of sodium hydroxide to increase the fatty acid solubility in boiling water under constant stirring. The content of the second beaker was then added into the first and stirred for 1 h until a foam layer of superhydrophobic calcium carbonate was formed on the surface of the water. The beaker was then placed in an oven for overnight to allow the water to completely evaporate. A cake of superhydrophobic powder was obtained; it was then gently crushed to yield the fine powder

Fatty acid was also used to treat the surface of a piece of natural, flat and colourless calcite crystal. Since the crystal has large flat surface, the fatty acid treated crystal was used for water contact angle measurement. It was thought that the water contact angle measurements on this flat fatty acid treated surface will provide the water contact angle value closer to the intrinsic water contact angle on calcium stearate.

2.3. Characterization of the fatty acid treated PCC

SEM images of the dried treated powder were obtained using a JEOL JSM-7001F FEGSEM (2008) scanning electron microscope (Fig. 1). Water and oil contact angles on fatty acid treated PCC and calcite crystal were measured using a Dataphysics OCA instrument and the results can be seen in (Fig. 2).

2.4. Study of selective absorption of oil from water

In oil–water separation study, two separate sets of experiments were done to investigate the separation of diesel and crude oil from water using superhydrophobic PCC. Oven dried superhydrophobic PCC was added to oil–water mixtures of varied weight ratios where it selectively absorbs the oil from the water. The oil–water mixture volume was kept constant as 100 ml in all the experiments, and the weight of the powder was kept the same as the weight of the oil in the mixture. The powder was sprinkled into the mixture afterward where it rapidly absorbed the oil while repelling the water. The clear water left after the oil and powder removal was then weighed and the absorption efficiency was measured as recovered water weight divided by initial water weight multiplied by 100.

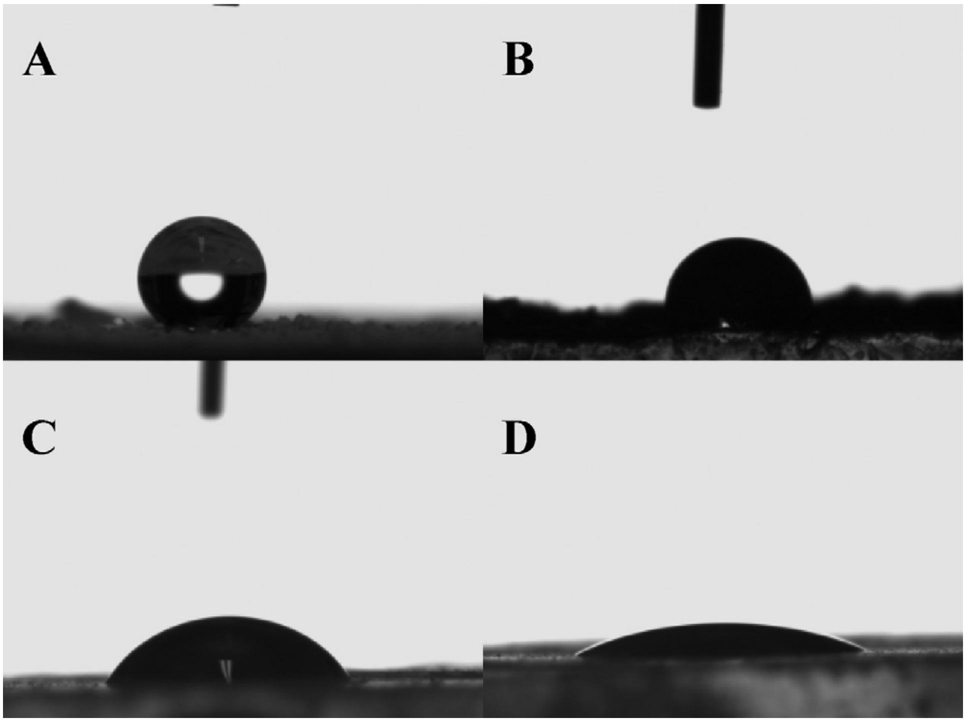

Fig. 2. A water droplet on (A) Powder fixed on a glass slide using a glue, contact angle (CA) = 152°; (B) a flat piece of calcite crystal, CA = 93°; (C) A diesel oil droplet, CA = 42°; (D) crude oil droplet on the flat piece of calcite crystal treated with stearic acid, CA = 25°.

3. Results and discussion

SEM images (Fig. 1) show that most of the precipitated calcium carbonate crystals are needle-shaped and have smooth surface. After the treatment with the stearic acid, an insoluble layer of calcium stearate is formed on the surface of the crystals and the crystal surface became rougher due to the erosion effect of the treatment.

In order to investigate the wetting behaviour of the treated powder (Fig. 2), two different approaches were employed for contact angle measurements. In the first measurement, a thin layer of powder was fixed on a glass slide after a thin layer of glue was applied on the surface. An apparent water contact angle of 152° was observed; this value is in agreement with that of a superhydrophobic surface. In the second measurement, the water contact angle for the fatty acid treated natural calcite crystal was measured. A water contact angle value of 92° was recorded. This contact angle value is closer to the expected water contact angle for a closely assembled stearate monolayer [22]. From these contact angle data, the area fraction of the water–air interface (i.e. $(1-\phi)$) can be calculated using the Cassie–Baxter model; for our data it was calculated to be 0.899. These water contact angle results are in agreement with the prediction of the Washburn model that water cannot penetrate into the capillary system of the stearic acid treated calcium carbonate powder.

In contrast, the diesel and crude oil samples formed contact angles of 42° and 25°, respectively, on the stearic acid treated calcite surface. Based on the Washburn model, both diesel and crude oil, having intrinsic contact angles of the above values, can penetrate the fatty acid treated calcium carbonate powder. We found that the apparent contact angles of diesel and crude oil on the stearic acid treated calcium carbonate powder mass could not be measured due to the rapid penetration of these oils into the powder mass.

The above water and oil penetration results indicated that if the fatty acid treated calcium carbonate powder is in contact of an oil–water mixture, oil will be absorbed by the powder mass whereas water will not. To qualitatively demonstrate the separation of oil from water using the treated calcium carbonate powder (Fig. 3), 10 g of diesel doped with a red dye (Sudan IV) was added to a beaker containing 90 g of water. Ten grams of treated calcium carbonate powder was then added into the beaker. The powder selectively absorbed the diesel, leaving clear water behind. The diesel-loaded powder can then be easily recovered from the water surface.

According to the Wenzel's equation [23] (Eq. (3)) the surface roughness of the powder mass further enhances the difference of water and oil wetting behaviour on the treated PCC powder.

$$\cos\theta_{\mathrm{r}} = r\cos\theta \tag{3}$$

Eq. (3) shows the Wenzel's model which defines the actual surface area available for a liquid to establish contact through wetting, where θ_{r} is the observed contact angle on a rough surface, r is the surface roughness factor which is the ratio of the actual contact area versus the projected contact area, and θ is the equilibrium contact angle on a smooth surface of the same material [21]. Under the Wenzel's model a liquid can access the surface areas of the troughs; a wetting liquid will have a lower contact angle on a rough surface than on a smooth material of the same material. However, a non-wetting liquid (i.e. $\theta > 90°$) is unable to fully access the troughs of a rough surface when the roughness factor r of the surface reaches a critical level and air pockets are formed in troughs. In such case, the wetting condition switches from the Wenzel regime to the Cassie regime and the liquid contact angle will increase with the increase in surface roughness. Therefore, the stearic acid treated calcium carbonate powder mass is more hydrophobic to water and at the same time more oleophilic to oil. The roughness enhanced changes in the wetting behaviour of oil and water on the treated PPC powder suggest that the powder should have high efficiency for selective absorption of oil from water. A quantitative study was performed to investigate the absorption efficiency by gravimetrically determining the amount of water being absorbed into the treated PCC powder out of the diesel and the crude oil samples of varied oil to water ratio (Table 1). The slight weight loss of water after the

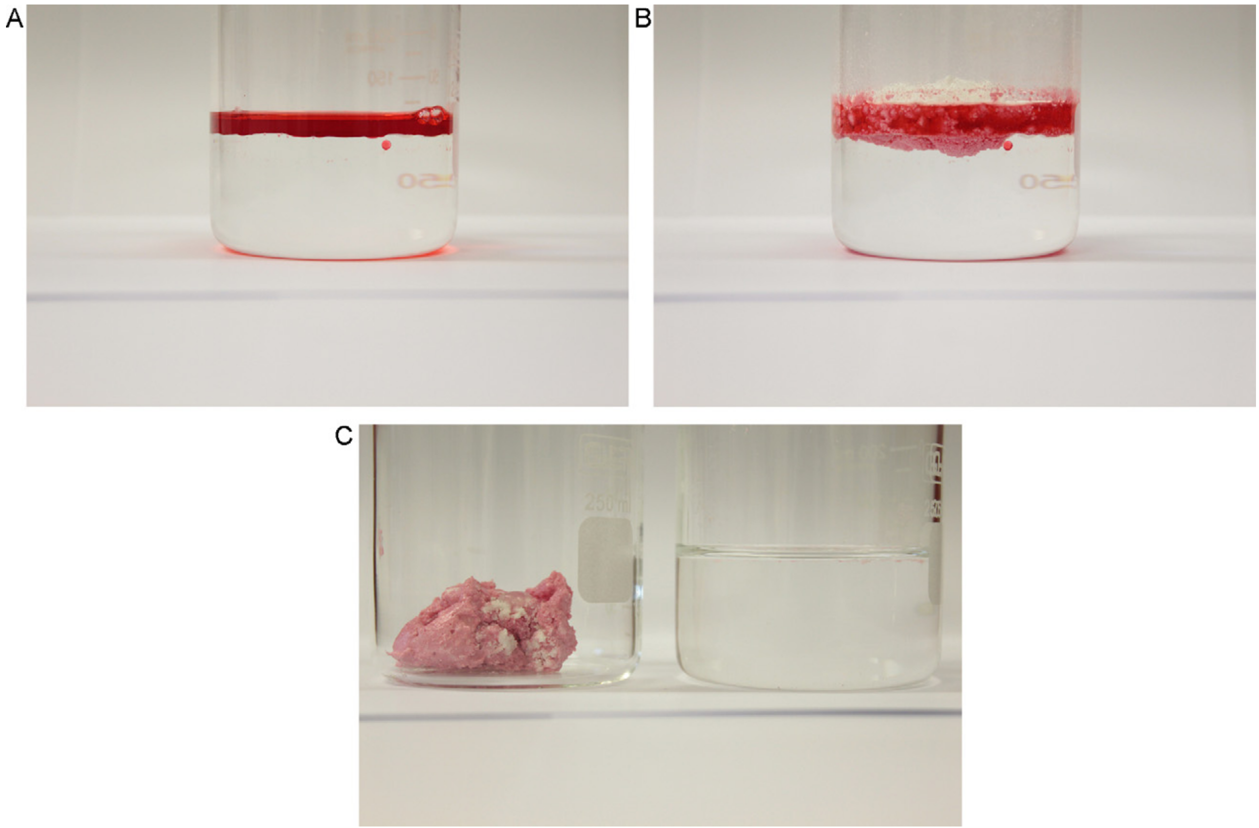

Fig. 3. Oil–water mixture (A) before powder addition; (B) right after powder addition; (C) after separation.

Table 1
The oil absorption efficiency (%) data calculated for crude oil and diesel oil.

Oil:water (w/w) ratio	Diesel oil–water	Crude oil–water
1:100	99.6%	99.5%
1:50	99.2%	99.1%
1:20	98.7%	98.9%
1:5	98.5%	98.2%
1:1	98.3%	98.1%

oil–water separation is most likely due to the absorption of water together with oil by the superhydrophobic powder mass.

Superhydrophobic PCC powder has three main advantages, which makes it a suitable candidate for oil absorption purposes: It is environmentally friendly, since calcium carbonate is also a natural material in the marine environment. It is low-cost, since the raw materials, i.e. PCC and fatty acids, are commodity industrial materials that are widely available. It is very easy to prepare compared to many other methods reported so far for the fabrication of superhydrophobic materials and is therefore also user friendly. As a result, fatty acid treated PCC is potentially a cost-effective material to be used either as a stand-alone method for controlling a patchy oil spill or to use in conjunction with other mainstream technologies for controlling more significant spills.

4. Conclusion

In this communication, the idea of using superhydrophobic and oleophilic powder as a selective oil sorbent against water was presented. Fatty acid treated calcium carbonate powder was characterized to have superhydrophobic and oleophilic properties. The treated calcium carbonate powder was found to be suitable for separating the oil from oil–water mixture and was able to achieve high separation efficiency. This low-cost, effective and environmentally friendly material makes a potential candidate for oil spill clean-ups. The preparation method of the superhydrophobic powder is simple, making the mass production of such powder possible. Further work will focus on the optimization of the powder properties and to investigate the factors influencing the rate of oil absorption process as well as further studies on oil recovery after separation.

Acknowledgements

This work is funded by the Australian Research Council. Funding received from ARC LP0989823 is gratefully acknowledged. In addition, TA would like to thank Monash University Research and Graduate School for postgraduate research scholarships. Mr A. Shirley of Shell Refining (Australia) is gratefully thanked for kindly providing the crude oil samples for this study. The authors also thank Dr. E. Perkins and Mr. D. Ballerini for proof reading of the manuscript, and acknowledge use of facilities within the Monash Centre for Electron Microscopy.

References

[1] X.-M. Li, D. Reinhoudt, M. Crego-Calama, What do we need for a superhydrophobic surface? A review on the recent progress in the preparation of superhydrophobic surfaces, Chemical Society Reviews 36 (2007) 1350–1368.
[2] N.J. Shirtcliffe, G. McHale, S. Atherton, M.I. Newton, An introduction to superhydrophobicity, Advances in Colloid and Interface Science 161 (2010) 124–138.
[3] A.B.D. Cassie, S. Baxter, Wettability of porous surfaces, Transactions of the Faraday Society 40 (1944) 546–551.
[4] A. Tuteja, W. Choi, J.M. Mabry, G.H. McKinley, R.E. Cohen, Robust omniphobic surfaces, Proceedings of the National Academy of Sciences of the United States of America 105 (2008) 18200–18205.
[5] J.-Y. Shiu, C.-W. Kuo, P. Chen, C.-Y. Mou, Fabrication of tunable superhydrophobic surfaces by nanosphere lithography, Chemistry of Materials 16 (2004) 561–564.

[6] H.Y. Erbil, A.L. Demirel, Y. Avci, O. Mert, Transformation of a simple plastic into a superhydrophobic surface, Science 299 (2003) 1377–1380.

[7] R. Fürstner, W. Barthlott, C. Neinhuis, P. Walzel, Wettting and self-cleaning properties of artificial superhydrophobic surfaces, Langmuir 21 (2005) 956–961.

[8] F. Feuillebois, M.Z. Bazant, O.I. Vinogradova, Effective slip over superhydrophobic surfaces in thin channels, Physical Review Letters 102 (2009) 1–4.

[9] H. Zhang, R. Lamb, J. Lewis, Engineering nanoscale roughness on hydrophobic surface – preliminary assessment of fouling behaviour, Science and Technology of Advanced Materials 6 (2005) 236–239.

[10] L. Feng, Z. Zhang, Z. Mai, Y. Ma, B. Liu, L. Jiang, D. Zhu, Super-hydrophobic and super-oleophilic coating mesh film for the separation of oil and water, Angewandte Chemie International Edition 43 (2004) 2012–2014.

[11] J. Zhang, W. Huang, Y. Han, A composite polymer film with both superhydrophobicity and superoleophilicity, Macromolecular Rapid Communications 27 (2006) 804–808.

[12] C.-W. Tu, C.-H. Tsai, C.-F. Wang, S.-W. Kuo, F.-C. Chang, Fabrication of superhydrophobic and superoleophilic polystyrene surfaces by a facile one-step method, Macromolecular Rapid Communications 28 (2007) 2262–2266.

[13] Q. Wang, Z. Cui, Y. Xiao, Q. Chen, Stable highly hydrophobic and oleophilic meshes for oil – water separation, Applied Surface Science 253 (2007) 9054–9060.

[14] S. Wang, Y. Song, L. Jiang, Microscale and nanoscale hierarchical structured mesh films with superhydrophobic and superoleophilic properties induced by long-chain fatty acids, Nanotechnology 18 (2007) 1–5.

[15] Q. Pan, M. Wang, H. Wang, Separating small amount of water and hydrophobic solvents by novel superhydrophobic copper meshes, Applied Surface Science 254 (2008) 6002–6006.

[16] J. Yuan, X. Liu, O. Akbulut, J. Hu, S.L. Suib, J. Kong, F. Stellacci, Superwetting nanowire membranes for selective absorption, Nature Nanotechnology 3 (2008) 332–336.

[17] C. Wang, T. Yao, J. Wu, C. Ma, Z. Fan, Z. Wang, Y. Cheng, Q. Lin, B. Yang, Facile approach in fabricating superhydrophobic and superoleophilic surface for water and oil mixture separation, ACS Applied Materials & Interfaces 1 (2009) 2613–2617.

[18] C. Lee, S. Baik, Vertically-aligned carbon nano-tube membrane filters with superhydrophobicity and superoleophilicity, Carbon 48 (2010) 2192–2197.

[19] S. Wang, M. Li, Q. Lu, Filter paper with selective absorption and separation of liquids that differ in surface tension, ACS Applied Materials & Interfaces 2 (2010) 677–683.

[20] H. Yang, P. Pi, Z.-Q. Cai, X. Wen, X. Wang, J. Cheng, Z. Yang, Facile preparation of super-hydrophobic and super-oleophilic silica film on stainless steel mesh via sol – gel process, Applied Surface Science 256 (2010) 4095–4102.

[21] A.W. Adamson, A.P. Gast, Physical Chemistry of Surfaces, 6th ed., John Wiley & Sons Inc., 1997.

[22] H. Tavana, A. Amirfazli, A.W. Neumann, Fabrication of superhydrophobic surfaces of n-hexatriacontane, Langmuir 22 (2006) 5556–5559.

[23] R.N. Wenzel, Resistance of solid surfaces to wetting by water, Industrial & Engineering Chemistry 28 (1936) 988–994.