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A fast and convenient cellulose hydrogel coated colander for high-efficiency oil/water separation†

Fei Lu, Yuning Chen, Na Liu, Yingze Cao, Liangxin Xu, Yen Wei, Lin Feng*

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Cellulose hydrogel is successfully prepared in alkali/urea solution using freezing/melting method and is coated on nylon mesh. The as-prepared mesh is superhydrophilic in air with a water contact angle of 0°and superoleophobic under water with an oil contact angle above 150°. The hydrophobicity maintains well in various aqueous phases, which reflects the stability in severe condition. The mesh is well utilized in oil/water separation. water could permeate through the mesh while oil was obstructed. The separation process runs efficiently without auxiliary power and a colander is also fabricated with the mesh for application in scooping waste oil.

Introduction

The treatment of oil pollution has always been a global issue which has attracted large amount of manpower and financial resources devoted on it [1-5]. Design of new materials for oil/water separation is a subject with good prospect to solve this problem, and significant progress is continuously made by researchers from worldwide range every year [6-10]. Traditional materials is often based on absorb mechanism [11-14] to separate oil from water, such as oil-absorb sponge [15-16]. Recently, materials with specific wettability [17-22] are found potential to be used for oil/water separation with high efficiency. Superoleophilic/superhydrophobic material could sustain water upside while let oil permeate through it [23-24]. On the other side, superhydrophilic/superoleophobic material could retard oil and simultaneously let water pass by [25-26]. Systemic theories have also been formed to explain the mechanism of wettability and interfacial phenomena [27-28]. These kinds of materials have offered a new direction to solve oil pollution problem.

Cellulose is a natural macromolecule that is widely used in food, fabric and medical industries [29-31]. Its low cost, hydrophilicity and good biocompatibility make it a promising material to be used in oil/water separation. In the field of water treatment, cellulose is often used as base material to produce oleophilic sponge with capacity to absorb floating oil [32]. However, this kind of sponge is easily fouled by waste oil and lacks efficiency when separating large volume of oil from aqueous phase. Therefore, to overcome this disadvantage and directed by the wettability theory, we have prepared a superhydrophilic and underwater superoleophobic mesh fabricated with cellulose gel and nylon. A colander with a handle has also been assembled as a model for further application.

* Department of Chemistry, Tsinghua University, Beijing, 100084, P. R. China. E-mail: fl@mail.tsinghua.edu.cn

† Electronic supplementary information (ESI) available.

Experimental

Materials

Nylon mesh and stainless steel wire were purchased from Huawei Hardware. China. Microcrystalline cellulose, sodium hydroxide, n-hexane and all other chemical reagent were purchased from Sinopharm Chemical Reagent Co., Ltd. China.

Fabrication of cellulose-coated mesh

Firstly, nylon mesh (mesh number: 100) was rinsed by acetone and deionized water in sequence. (10 minutes each). Then, 18g thio urea, 24g sodium oxide and 15g microcrystalline cellulose was mixed with 300 mL deionized water to form a milk-like mixture. The mixture was frozen at -20 ℃ for 12 hours and melted at room temperature subsequently to form clear cellulose solution. 6 mL epoxy chloropropane was then added into the solution as crosslink agent. After stirred for 5 min at 600 rpm, nylon mesh was immersed into the solution and the mixture was freezing at -20 ℃ for 12 hours then melting at room temperature again. Thus the gelation step was finished and the nylon mesh was wrapped by cellulose hydrogel. After removal of the redundant hydrogel, rinsing with deionized water and drying at 40℃, the cellulose-gel-coated nylon mesh was obtained.

Characterization

Measurement of WCA and OCA were performed with OCA20 Contact Angle System (Dataphysics, Germany). WCA was measured directly on the sample table with water syringe, all samples should be pre-dried. OCA was measured in cubic glass box filled with aqueous phase, 1,2-dichloroethane was used as oil droplet. SEM images were taken by Phenom Pro scanning electron microscope (FEI). Measurement of oil concentration was performed with OIL480 infrared oil analyser (HuaxiaKechuang, China).

Results and discussion

The hydrophilic property of cellulose is usually attributed to the hydroxyl group in its molecular structure. However, the compact crystal structure of cellulose makes it difficult to dissolve in customary organic and inorganic solvents. In order to produce hydrogel, it is necessary to form a stable aqueous solution of cellulose. Several kinds of solvent have already been designed [33-35] and each of them could dissolve cellulose successfully in different concentration level. Since cellulose hydrogel is proposed to be used to make the colander, we've chosen the alkali/urea aqueous system [36] as the solvent of cellulose, in which thio urea and sodium hydroxide were used. After a freezing/melting procedure, cellulose was dissolved as expected.

It is well known surface wettability is influenced by both surface energy and surface roughness [27-28]. Therefore, nylon mesh with a mesh number of 100 was used as the substrate to form the strainer part of the colander. The substrate also introduced a micron-sized porous structure to the surface, which increased surface roughness. Epoxy chloropropane was added to the cellulose solution as crosslinking agent, then nylon mesh was immersed into the solution. After another freezing/melting procedure, cellulose hydrogel was formed with nylon mesh inside of it. Redundant hydrogel was removed and thus a nylon mesh coated with cellulose gel was successfully prepared. As shown in Fig.1, the nylon fibre was smoothly coated with cellulose gel. Meanwhile, the pore was left unrestricted for water to pass through.

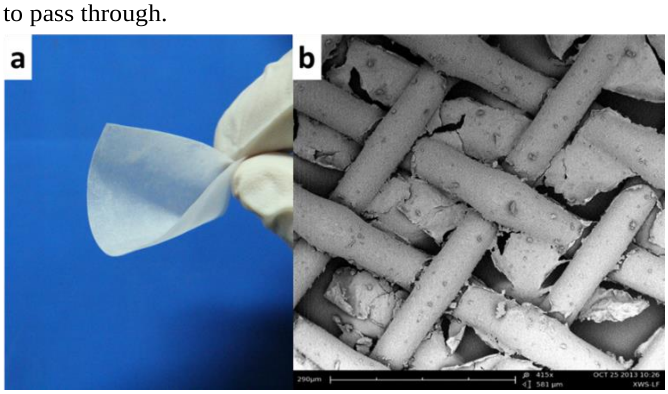

Fig.1 a) A macro view of the as prepared cellulose-coated nylon mesh, which is very soft. b) Typical SEM image of cellulose-coated nylon mesh. The surface of nylon fibre was covered by cellulose hydrogel and the pores were left unblocked.

After drying in the air, the as-prepared mesh shows excellent superhydrophilicity with a water contact angle (WCA) of 0 °(Fig. 2a). In previous studies of superhydrophilic/superoleophobic mesh [37-39], the capacity to maintain water is believed to be a key parameter when evaluating the ability for oil/water separation, and low WCA means the mesh could maintain water easily. When immersed in water, the mesh shows good oil repellency with an oil contact angle (OCA) beyond 150 °(Fig. 2b), which is a typical parameter of "superoleophobic". It is usually hypothesized [13] that in aqueous phase, it is the water on the mesh's surface that directly contacts with the oil droplet instead of the mesh itself. Thus, the mesh's superhydrophilicity in air is just the causal factor of the superoleophobicity underwater. In other words, good water affinity means good oil repellency. As described above, our study's result just supports this hypothesis (Fig. 2).

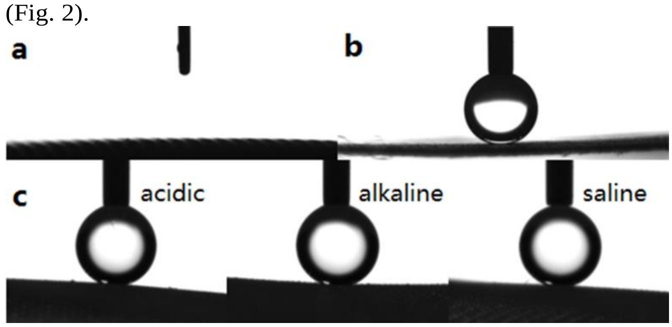

Fig. 2. Contact angle of the cellulose hydrogel coated mesh. The mesh is a) superhydrophilic in air with WCA of 0°and b) superoleophobic underwater with OCA above 150°. 1, 2-dichloroethane was used as oil droplet. c) The mesh could sustain superoleophobicity in alkaline (0.1 mol/L sodium hydroxide), acidic (0.1 mol/L muriatic acid) and saline aqueous (1 mol/L sodium chloride) phases.

Typically, waste water often has complex composition. Therefore, our mesh should be stable in aqueous phase with serious condition so as for application. To test its stability in water, alkaline (0.1 mol/L sodium hydroxide), acidic (0.1 mol/L muriatic acid) and saline aqueous (1 mol/L sodium chloride) phases were chosen. The result (Fig. 2c) shows that the mesh could sustain its superoleophobicity in all these kinds of aqueous phases with OCA above 150 °, which means it is suitable to be used for oil/water separation.

The experiment of oil/water separation was operated with the device shown in Fig. 3. The as-prepared mesh was firstly cut to 5×5 cm^2 and then fixed with a clamp made of polytetrafluoroethylene (PTFE). A glass tube was fixed upside as the entrance of oil/water mixture and a beaker downside as the accepter of the filtered liquid. 60 mL mixture of n-hexane (dyed with oil red) and deionized water (1:1 v/v) was poured into the glass tube (Fig. 3a). As expected, n-hexane was successfully blocked upside and water could permeate though the mesh almost instantaneously (Fig. 3b) within 10 seconds.

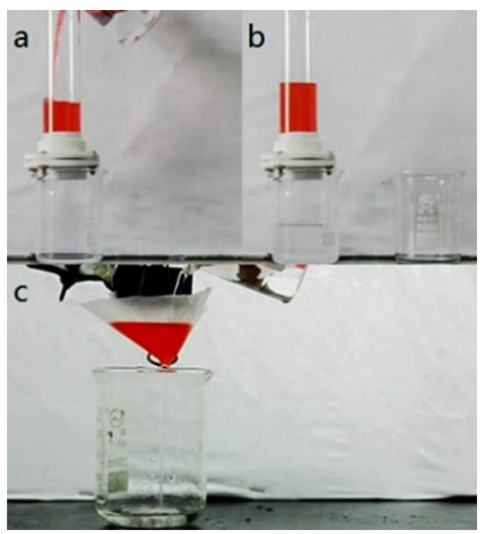

Fig. 3 a) The device for oil/water separation is consist of a glass tube, a PTFE clamp and a 100 mL beaker. The mesh was fixed by the clamp and 60mL oil/water mixture (n-hexane : water=1:1, v/v) was poured into the glass tube. b) After the separation, oil was sustained upside and water passed through the mesh to the beaker. c) A clear view during the separation. Water passed the mesh instantaneously while oil (n-hexane dyed by oil red) was blocked upside.

To evaluate the separation efficiency and get a clear view of the separation, we also made a cone-shape filter with the mesh and repeated the oil/water separation process with 20 mL n-hexane (dyed by oil red) and 40mL deionized water (Fig. 3c). It could be seen clearly that there is not a bit of oil permeating through the mesh and no water was obstructed upside even during fast pour. Visually, the water spouts upside and downside the filter has nearly the same diameter as if there was no mesh intercepting the water (Movie S1 in Supplementary Information). Hence, nylon mesh coated with cellulose hydrogel is proved to be an appropriate material for oil/water separation with high efficiency.

We've also carried on an oil-concentration test with the device shown in Fig.3a. 50mL of different kinds of oil (n-hexane, petro-ether, gasoline, and diesel) were used as the oil phase. Firstly, the oil phase was mixed with 100 mL deionized water. Then, both of them were poured into the glass tube. After the separation finished, oil concentration of the aqueous phase in the beaker was tested with an infrared oil analyser. As shown in Fig.4a, the oil concentration was extremely low in each of the 4 water samples. As for the mixture of hexane/water or petro-ether/water, the oil concentration was less than 10mg/L. For mixture of gasoline/water and diesel/water, the oil concentration was around 300mg/L. We've also calculated the separation efficiency using the equation below:

$$E = 1 - C/C_0$$

In this equation, *E* represents the separation efficiency, *C* stands for the oil concentration in the water samples after separation and C_0 is for the equivalent oil concentration of the mixture before separation. As shown in Fig.4b, the separation efficiency was as high as 99.99%. Thus we were confirmed that the mesh could successfully separate various kinds of oil/ water mixture with high efficiency.

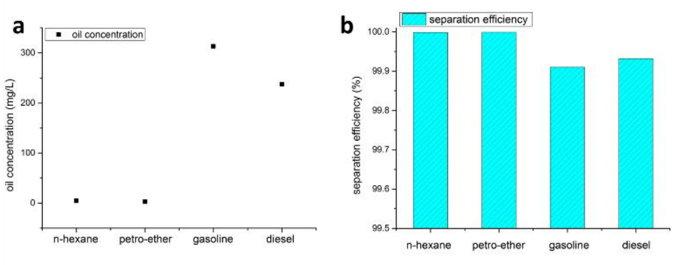

Fig. 4 a) The oil concentration of water samples after separation, in which different kinds of oil/water mixture were used (hexane/water, petro-ether/water, gasoline/water and diesel/water). b) The separation efficiency calculated with the equation: $= 1 - C/C_0$, E for the separation efficiency, *C* for the oil concentration in the water samples after separation and C_0 for the equivalent oil concentration of the mixture before separation.

Using the as-prepared mesh and stainless steel wire, we've also assembled a colander model with sewing cotton for prospective application. (Fig. 5a) The spoon-like colander with a handle could be used to scoop oil from water (100 mL n-hexane with oil red and 270 mL deionized water). Because water could quickly permeate through, the colander could efficiently collect the oil floating on water (Movie S2/S3 in Supplementary Information). After several times of scooping, oil was gathered in another beaker along with tiny amount of water that can't be percept visually (Fig. 5b). The mesh has several advantages such as stability, low cost of raw material and simple production method. Taking these advantages into consideration, the colander could promisingly be applied in industry as well as daily life.

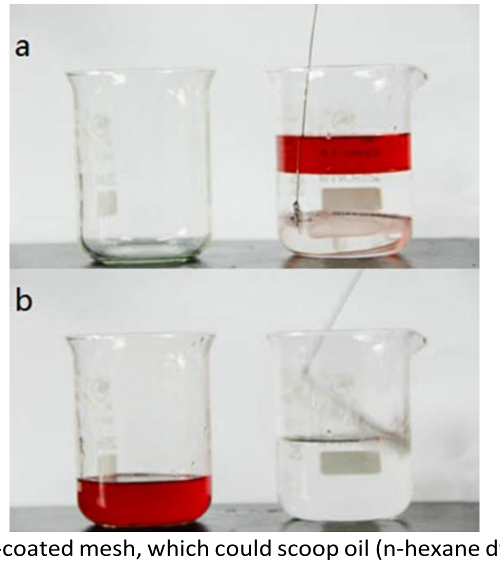

Fig. 5 a) A colander model made of stainless steel wire and cellulose-coated mesh, which could scoop oil (n-hexane dyed by oil red) from water. b) After several times of scooping, oil/water mixture was separated and oil was collected to the other beaker with imperceptible amount of water inside.

The mesh was preserved in deionized water to maintain its superhydrophilicity. Water could also separate the mesh from air. Thus the mesh is not easily fouled by airborne pollutant. Every time after oil/water separation experiment, the mesh was cleaned with deionized water and kept in water subsequently. This preservation method makes the mesh suitable for cycling use. In the oil-concentration test described in Fig.4, all the tests were operated with the same mesh, which means the mesh could efficiently separate oil from water after 12 times of cycling use. After kept in water for 90 days, this mesh could still maintain its underwater superoleophobicity. As shown in Fig.6a, the oil contact angle is 154 °. Except from its advantage for cycling use, the mesh is also vary stable. The mesh's size is 5*5cm^2, and the weight is 0.168g. As shown in Fig.6b, the mesh could sustain large volume of oil (110 mL n-hexane). The oil's weight is 72.5g, which means the mesh could sustain oil 432 times of its own weight. The oil's height in Fig.6b is 19.5cm, thus we could calculate that the pressure is 1260Pa. Because the glass tube in the picture is the longest one in our lab, this data (432 times of its weight, 1260Pa) has not reached the threshold of the mesh. However, it is enough to convince us that the mesh is very stable.

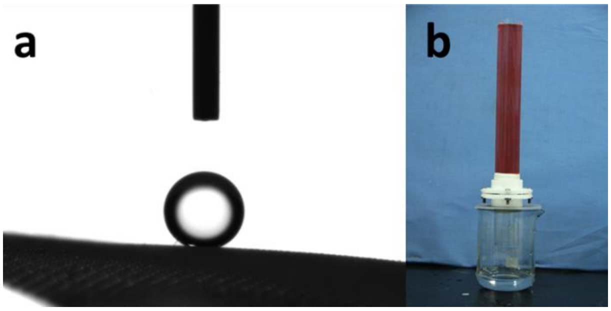

Fig.6 a) the mesh could maintain its underwater superoleophobicity after 12 times of cycling use and kept in water for 90 days. The oil droplet is 1,2-dichloroethane, and the oil contact angle is 154 °. b) After oil/water separation, the mesh could sustain 110mL n-hexane (dyed with oil red) upside. The oil's height is 19.5cm and the pressure on the mesh is 1260Pa.

Conclusion

In summary, we have fabricated a cellulose-coated nylon mesh. Because of the hydrophilicity of cellulose, the hydrogel coated mesh is superhydrophilic in air and superoleophobic under water. This special wettability makes it suitable for oil/water separation. Water could pass through it quickly while oil was obstructed upside. A colander model was also made with the mesh. It could be used to scoop oil from water. The mesh has advantages such as stability, low cost and simple production method. It has prospective applications in daily life.

Acknowledgements

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References

1 L. P. Gossen, L. M. Velichkina, *Pet. Chem.* 2006, **46**, 67-72.
2 A. Bayat, S. F. Aghamiri, A. Moheb, G. R. Vakili-Nezhaad, *Chem Eng Technol* 2005, **28**, 1525-1528.
3 L. C. Osuji, C. M. Onojake, *Chemistry & Biodiversity* 2004, **1**, 1708-1715.
4 J. M. Baker, *Pure Appl Chem* 1999, **71**, 135-151.
5 A. B. Nordvik, J. L. Simmons, K. R. Bitting, A. Lewis, T. StromKristiansen, *Spill Sci Technol B* 1996, **3**, 107-122.
6 M. Inagaki, A. Kawahara, Y. Nishi, N. Iwashita, *Carbon* 2002, **40**, 1487-1492.
7 M. Toyoda, K. Moriya, J. Aizawa, H. Konno, M. Inagaki, *Desalination* 2000, **128**, 205-211.
8 A. Bayat, S. F. Aghamiri, A. Moheb, G. R. Vakili-Nezhaad, *Chem Eng Technol* 2005, **28**, 1525-1528.
9 S. Kalia, B. S. Kaith, I. Kaur, *Polym Eng Sci* 2009, **49**, 1253-1272.
10 T. T. Lim, X. F. Huang, *Chemosphere* 2007, **66**, 955-963.
11 S. H. Kim, I. D. Chung, C. S. Ha, K. J. Kim, W. J. Cho, *J Appl Polym Sci* 1999, **73**, 2349-2357.
12 J. Jang, B. S. Kim, *J Appl Polym Sci* 2000, **77**, 914-920.
13 M. H. Zhou, W. J. Cho, *Polym Int* 2001, **50**, 1193-1200.
14 A. M. Atta, R. A. El-Ghazawy, R. K. Farag, A. F. El-Kafrawy, A. A. A. Abdel-Azim, *Polym Int* 2005, **54**, 1088-1096.
15 D. Cho, H. N. Chang, *Korean J Chem Eng* 1998, **15**, 445-448.
16 V. O. A. Tanobe, T. H. D. Sydenstricker, S. C. Amico, J. V. C. Vargas, S. F. Zawadzki, *J Appl Polym Sci* 2009, **111**, 1842-1849.
17 H. J. Li, X. B. Wang, Y. L. Song, Y. Q. Liu, Q. S. Li, L. Jiang, D. B. Zhu, *Angew Chem Int Edit* 2001, **40**, 1743-1746.
18 L. Feng, S. Li, Y. Li, H. Li, L. Zhang, J. Zhai, Y. Song, B. Liu, L. Jiang, D. Zhu, *Adv Mater* 2002, **14**, 1857-1860.
19 X. J. Feng, L. Jiang, *Adv Mater* 2006, **18**, 3063-3078.
20 J. K. Yuan, X. G. Liu, O. Akbulut, J. Q. Hu, S. L. Suib, J. Kong, F. Stellacci, *Nature Nanotechnology* 2008, **3**, 332-336.
21 U. Manna, M. C. D. Carter, D. M. Lynn, *Adv Mater* 2013, **25**, 3085-3089.
22 Y. Cao, X. Zhang, L. Tao, K. Li, Z. Xue, L. Feng, Y. Wei, *Acs Applied Materials & Interfaces* 2013, **5**, 4438-4442.
23 L. Feng, Z. Y. Zhang, Z. H. Mai, Y. M. Ma, B. Q. Liu, L. Jiang, D. B. Zhu, *Angew Chem Int Edit* 2004, **43**, 2012-2014.
24 Z. Xue, Z. Sun, Y. Cao, Y. Chen, L. Tao, K. Li, L. Feng, Q. Fu, Y. Wei, *Rsc Advances* 2013, **3**, 23432-23437.
25 Z. X. Xue, S. T. Wang, L. Lin, L. Chen, M. J. Liu, L. Feng, L. Jiang, *Adv Mater* 2011, **23**, 4270-4273.
26 D. L. Tian, X. F. Zhang, Y. Tian, Y. Wu, X. Wang, J. Zhai, L. Jiang, *J Mater Chem* 2012, **22**, 19652-19657.
27 R. N. Wenzel, *Industrial and Engineering Chemistry* 1936, **28**, 988-994.
28 A. B. D. Cassie, S. Baxter, *Transactions of the Faraday Society* 1944, **40**, 0546-0550.
29 E. W. Crampton, L. A. Maynard, *J Nutr* 1938, **15**, 383-395.
30 H. P. Chin, Blankenh.Dh, *Clin Chim Acta* 1968, **20**, 305-&.
31 L. Dall'Acqua, C. Tonin, R. Peila, F. Ferrero, M. Catellani, *Synthetic Met* 2004, **146**, 213-221.
32 J. T. Korhonen, M. Kettunen, R. H. A. Ras, O. Ikkala, *Acs Applied Materials & Interfaces* 2011, **3**, 1813-1816.
33 R. P. Swatloski, S. K. Spear, J. D. Holbrey, R. D. Rogers, *J Am Chem Soc* 2002, **124**, 4974-4975.
34 J. Cai, L. Zhang, *Macromol Biosci* 2005, **5**, 539-548.
35 S. D. Zhu, Y. X. Wu, Q. M. Chen, Z. N. Yu, C. W. Wang, S. W. Jin, Y. G. Ding, G. Wu, *Green Chem* 2006, **8**, 325-327.
36 M. Egal, T. Budtova, P. Navard, *Cellulose* 2008, **15**, 361-370.
37 F. Zhang, W. B. Zhang, Z. Shi, D. Wang, J. Jin, L. Jiang, *Adv Mater* 2013, **25**, 4192-4198.
38 N. Liu, Y. Chen, F. Lu, Y. Cao, Z. Xue, K. Li, L. Feng, Y. Wei, *Chemphyschem* 2013, **14**, 3489-3494.
39 C. Gao, Z. Sun, K. Li, Y. Chen, Y. Cao, S. Zhang, L. Feng, *Energy & Environmental Science* 2013, **6**, 1147-1151.